On a laboratory scale, beryllium is prepared by electrolysis of a mixture of molten beryllium fluoride and alkali or alkaline earth fluorides. The product obtained is 99.7% pure; the commercial material obtained by the same method is < 99%. Industrial electrolysis of beryllium chloride-alkali chloride melts yields beryllium with a purity usually greater than 99.8%.

Very high purity Be is obtained by Kroll’s procedure (which is a modification of Sloman’s method) which consists in vacuum distillation in the apparatus shown in Fig. 252. The relatively impure beryllium is placed in a BeO crucible and induction heated, and its vapor is condensed in a condensation hood. The latter is tightly joined to the crucible, but has an opening on top, so that the course of the distillation may be observed through a quartz peephole at the top of the apparatus. The BeO crucible is embedded in sintered, powdered BeO which fills a retaining vessel of sintered alumina.

The whole assembly is placed in a quartz tube which is closed off on top by a special water-cooled adapter. This metallic adapter may be made either of compressed metal powder or of bronze impregnated with tin under vacuum. It is sealed to the quartz tube with high-vacuum silicone grease. The apparatus is connected to a high-vacuum pump by means of a flexible tombac tube. The distillation requires a vacuum of < $10^{-3}$ mm.

The distillation of crude beryllium is connected with certain difficulties since the metal occludes the electrolyte and alkaline earth metals. These may cause bubbling and spattering of the metallic melt during the distillation. Therefore, preliminary degassing is carried out without the condensation hood until gas evolution ceases. After cooling, the condensation hood is installed, and after high vacuum has been restored the distillation is carried out at a temperature of 1400 to 1500°C. If beryllium flakes are used, they are first compressed and melted. This melt may be
distilled at once since it does not contain salt occlusions. The distillation is complete in about 20 minutes. The run is ended when about 75% of the charge has distilled. Depending on the operating temperature, the beryllium collects on the hood in the form of large globules or an incrustation (dendrites). The degree of purity should exceed 99.97%, neglecting the small quantity of oxygen that may be present.

The recovery of Be compounds from gadolinite is described in the section on scandium, yttrium and rare earth metals.

PROPERTIES:

Atomic weight 9.02.
M.p. 1280°C, b.p. 2970°C; crystallizes in structure type A3; brittle at room temperature, ductile at red heat.

In contact with water, Be becomes covered with a thin oxide layer but is not attacked further; however, it dissolves very vigorously in dilute acids.

REFERENCES:
H. Funk, Die Darstellung der Metalle im Laboratorium [The Preparation of Metals in the Laboratory], Stuttgart, 1938, p. 28.
W. Kroll, Metallwirtschaft 13, 725 (1934); Metal, Ind. 47, 29 (1935).
Beryllium Chloride

\( \text{BeCl}_2 \)

1. \( \text{BeO} + \text{C} + \text{Cl}_2 = \text{BeCl}_2 + \text{CO} \)

Beryllium halides do not attack Pyrex glass if the temperature is carefully controlled. Therefore, only the actual reaction apparatus must be of quartz, while vacuum sublimation and bottling may be carried out in Pyrex glass.

As shown in Fig. 253, the apparatus consists of a large quartz tube \( A \) (25-mm. diameter, 400 mm. long), which is connected with a gas drying system by means of a large ground glass joint; its other end is connected, by means of a small ground glass joint \( \alpha \), with a Pyrex apparatus. The latter consists of several cylindrical chambers \( B, C, D \) and \( E \) which serve as receivers and resublimation vessels for the halide. Chamber \( D \) is fitted with a side tube closed off by a breakable bulb. A system of storage bulbs (1, 2, 3, 4) is later sealed to the side arm.

An intimate blend of 3.5 g. of BeO and 2.5 g. of charcoal made from calcined sugar is charged into a quartz boat \( s \), which is then pushed into tube \( A \). After removal of water and other impurities adsorbed on the carbon by heating to about 900°C in a stream of \( \text{N}_2 \), the nitrogen is replaced by \( \text{Cl}_2 \) and the reaction temperature is adjusted to 700°C. The sublimate of \( \text{BeCl}_2 \), which collects over a period of several hours, forms beautiful white, matted crystals in the rear section of tube \( A \). After completion of the reaction, pure \( \text{N}_2 \) is reintroduced and the Pyrex apparatus is connected to joint \( \alpha \). The latter is not greased since no vacuum is applied. By proper positioning of the tubular furnace, the halide resublimes and deposits in the first chamber \( B \), while leaving a residue in \( A \). The sublimation takes place at an adequate rate at 380°C. Joint \( \alpha \) is then melt-sealed at its narrowest point and the apparatus is connected to the high-vacuum pump. A forerun is then sublimed into the fourth chamber \( E \) by shifting the furnace.
The furnace is then shifted back and the bulk of the material is sublimed into chamber \( C \). This may be done at 330\(^\circ\)C, provided a high vacuum is maintained. Chamber \( D \), still containing a residue, is removed by sealing off.

The material is then resublimed from \( C \) into \( D \). Thus, only chamber \( D \), completely evacuated and sealed off on both sides, remains of the entire Pyrex apparatus. The vacuum pump must operate continuously during these sublimations since it has been found impossible to carry them out in an evacuated and sealed apparatus. Small amounts of gas are desorbed from the glass walls, thus decreasing the vacuum. This in turn raises the sublimation temperature. At these higher temperatures, traces of BeCl\(_2\) react with the glass, forming \( \text{BeO} + \text{SiCl}_4 \), which again leads to deterioration of the vacuum until the sublimation ceases altogether and liquid SiCl\(_4\) forms at the coldest spot. It is best to carry out the entire operation without interruption over a period of about 30 hours.

To bottle BeCl\(_2\), a 10-cm.-long glass tube is attached to the side tube of \( D \), a small glass-covered steel rod \( b \) is pushed in, and finally the four-bulb assembly is sealed on. The apparatus is connected to the vacuum pump via a ground-glass joint, a cold trap and a stopcock. After thorough heating, the stopcock is closed, the apparatus is detached from the pump, and the little glass bulb is broken by moving \( b \) with a magnet. The beryllium chloride is sublimed into the individual bulbs at the highest vacuum obtainable, while the trap is cooled with liquid nitrogen; this operation requires about four hours per bulb.

**Other preparative methods:** The reaction of beryllium with Cl\(_2\) and \( \text{HCl (II)} \) or the treatment of BeO with \( \text{CCl}_4 \) (III) may also be recommended.

**Properties:**

Snow-white crystals or crystalline mass. M.p. 405\(^\circ\)C, b.p. 488\(^\circ\)C; d 1.90. Extremely hygroscopic; dissolution in water is highly exothermic. The solution is strongly acid due to hydrolytic cleavage. On evaporation, the hydrate \( \text{BeCl}_2 \cdot 4\text{H}_2\text{O} \) crystallizes in monoclinic, deliquescent platelets if the hydrolysis is depressed by the addition of hydrochloric acid; otherwise, basic chlorides precipitate. Anhydrous BeCl\(_2\) is readily soluble in alcohol and ether.

**References:**

Beryllium Bromide

**BeBr**

I. \[ \text{BeO} + \text{C} + \text{Br}_2 = \text{BeBr}_2 + \text{CO} \]

<table>
<thead>
<tr>
<th>Component</th>
<th>Molecular Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>BeO</td>
<td>25.0</td>
</tr>
<tr>
<td>C</td>
<td>12.0</td>
</tr>
<tr>
<td>Br₂</td>
<td>159.8</td>
</tr>
<tr>
<td>BeBr₂</td>
<td>168.8</td>
</tr>
<tr>
<td>CO</td>
<td>28.0</td>
</tr>
</tbody>
</table>

The directions for the preparation of BeCl₂ apply with the following modifications: a nitrogen stream charged with Br₂ vapor is passed over the BeO + C mixture at 1200°C. This mixture is very corrosive to quartz. The first sublimation may be completed sufficiently rapidly at atmospheric pressure at 360°C; for the following sublimations a temperature of 310°C is sufficient, provided a high vacuum is maintained.

II. \[ \text{Be} + \text{Br}_2 = \text{BeBr}_2 \]

<table>
<thead>
<tr>
<th>Component</th>
<th>Molecular Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Be</td>
<td>9.0</td>
</tr>
<tr>
<td>Br₂</td>
<td>159.8</td>
</tr>
<tr>
<td>BeBr₂</td>
<td>168.8</td>
</tr>
</tbody>
</table>

To prepare BeBr₂ directly from the elements, bromine is evaporated in a flask by heating with an infrared lamp and passed in a stream of argon over Be powder in a quartz tube at a temperature of 550°C. The end of the tube protrudes into a cold receiver consisting of a large glass cylinder. In order to avoid plugging of the tube in the transition zone, the interior of the tube is heated with an electrical winding to 450-500°C; the winding is surrounded by a small quartz tube which is sealed at one end. This quartz tube extends from the receiver into the hot zone of the reaction tube. The receiver is separated from the atmosphere by several wash bottles, which also serve as bubble counters.

The anhydrous bromide product is transferred to storage vessels under an inert gas blanket. The yield is 200-250 g. in six hours.

**PROPERTIES:**

Long, white needles. M.p. 488°C, with sublimation beginning at 360°C; d 3.47. Very hygroscopic; large heat of solution. The tetrahydrate crystallizes as rod-shaped, hygroscopic crystals when the BeBr₂ solution is evaporated to a sirupy consistency. Gaseous HBr must be added to the solution to avoid precipitation of basic salts due to hydrolysis.
REFERENCES:


Beryllium Iodide

\( \text{BeI}_2 \)

I. \[ \text{Be} + \text{I}_2 = \text{BeI}_2 \]

<table>
<thead>
<tr>
<th>Be</th>
<th>I₂</th>
<th>BeI₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.0</td>
<td>253.8</td>
<td>262.8</td>
</tr>
</tbody>
</table>

Beryllium iodide is formed via the reaction of gaseous \( \text{I}_2 \) (or a mixture of pure \( \text{H}_2 \) and \( \text{I}_2 \)) with metallic \( \text{Be} \) in a quartz tube at dull red heat. It is best to work in a sealed tube; however, the metal and the solid iodine should not be blended with each other, since this may cause bursting of the tube during heating. The metal is inserted separately in a glass container so that it comes in contact only with the \( \text{I}_2 \) vapor. After 2-3 days at 480°C, little unreacted iodine remains. Thus, each tube contains 4 g. of Be (1.8 g. excess) and 63 g. of iodine. The subsequent sublimation, which gives a pure white product, is carried out as described for \( \text{BeCl}_2 \); however, it is preferable to work in all-quartz equipment in view of the higher temperatures.

II. \[ \text{Be}_2\text{C} + 2\text{I}_2 = 2\text{BeI}_2 + \text{C} \]

\[
\begin{array}{c|ccc}
\text{Be}_2\text{C} & \text{I}_2 & \text{BeI}_2 & \text{C} \\
30.0 & 507.7 & 525.7 & 12.0
\end{array}
\]

\[ \text{Be}_2\text{C} + 4\text{HI} = 2\text{BeI}_2 + \text{CH}_4 \]

\[
\begin{array}{c|ccc}
\text{Be}_2\text{C} & \text{HI} & \text{BeI}_2 & \text{CH}_4 \\
30.0 & 511.7 & 525.7 & 16.0
\end{array}
\]

The iodide cannot be prepared in the same fashion as the chloride, i.e., by passing a nitrogen stream charged with \( \text{I}_2 \) over a mixture of \( \text{BeO} + \text{C} \); \( \text{Be}_2\text{C} \) is required as the starting material.

In a quartz tube at about 700°C, \( \text{Be}_2\text{C} \) is allowed to react with carefully purified and dried HI or with a hydrogen stream containing \( \text{I}_2 \) vapor. The subsequent purification by sublimation is the same as that described above for \( \text{BeCl}_2 \).

PROPERTIES:

White needles. M.p. 480°C, b.p. 488°C. Very hygroscopic; hydrolyzes vigorously, evolving HI.
REFERENCES:


Beryllium Oxide and Beryllium Carbonate

\[
\text{BeCO}_3 = \text{BeO} + \text{CO}_2
\]

Commercial beryllium carbonate, which usually contains more than 1% of impurities, is mixed in a platinum vessel with hot, twice-distilled acetic acid and the hot solution is filtered through a platinum Gooch crucible. The basic acetate separates as fine crystals on rapid chilling; it is recrystallized from glacial acetic acid three times. Each time, the salt is separated by means of a platinum basket centrifuge. After this preliminary purification, the acetate is sublimed at a temperature of 250°C in a large-diameter glass tube with a stream of pure, dry air flowing through the apparatus. The sublimate is heated in a degassed Pyrex flask with pure concentrated nitric acid to convert it to the nitrate. The latter may be calcined to the oxide at 1100°C; however, the oxide thus prepared always contains about 0.35 ml. of gas (N\(_2\), O\(_2\)) per gram of substance.

Very pure oxide may be obtained when the beryllium nitrate prepared as described above is reconverted to the carbonate. An acid solution of the nitrate is evaporated in a platinum dish to remove excess acid, the residue is dissolved in some water, and enough distilled ammonium carbonate solution is added to redisolve the initially precipitated beryllium carbonate and give a clear solution. The solution is then evaporated in a platinum dish until all the beryllium carbonate has separated as a coarse precipitate. After thorough washing with pure water and then with freshly distilled alcohol, the product is dried and finally calcined to the oxide in a platinum vessel placed in an electric furnace at 900°C.

PROPERTIES:

White, loose powder. M.p. 2530°C; d 29. Very sparingly soluble in water (about 0.20 g. per liter). Its solubility in acids depends upon the calcination temperature; dissolves most readily in hydro-fluoric acid. Crystallizes in structure type B4.
Beryllium Hydroxide

Be(OH)$_2$

Two crystalline modifications may be obtained, the metastable $\alpha$-Be(OH)$_2$ and the stable $\beta$-Be(OH)$_2$.

$\alpha$-Be(OH)$_2$

The $\alpha$ form is the primary product of aging of amorphous beryllium hydroxide, which is obtained by the precipitation of a beryllium salt solution with ammonia in the absence of CO$_2$; $\alpha$-Be(OH)$_2$ is then obtained by prolonged heating (about 24 hours) of the amorphous precipitate with 10% ammonium hydroxide solution.

A very pure material may be obtained by electrodialysis of amorphous beryllium hydroxide. This is a slow procedure and takes several days.

$\beta$-Be(OH)$_2$

The beta modification is best prepared by slow hydrolysis of sodium beryllate. Boiling 10N NaOH solution is saturated with pure, amorphous beryllium hydroxide until a permanent turbidity is just evident. A sandy, finely crystalline product separates upon slow cooling. Under the microscope, the crystals appear as beautiful, regular double pyramids. They may be purified, without changing their appearance, with warm water until they no longer show an alkaline reaction; the crystals are then dried at 80°C.

The same mother liquor may be reused several times in the saturation and crystallization sequence.

PROPERTIES:

Formula weight 43.04. d 1.92. Crystalline beryllium hydroxide is very slightly soluble in water and in dilute alkali. Both forms are readily soluble in hot concentrated sodium hydroxide.

REFERENCES:
R. Fricke and G.F. Huttig, Hydroxyde und Oxydhydrate [Hydroxides and Hydrated Oxides], Leipzig 1937, p. 12, as well as the literature cited there.
17. ALKALINE EARTH METALS

Sodium Beryllates

I. Concentrated sodium hydroxide saturated with beryllium hydroxide, or alcoholic potassium hydroxide saturated with potassium beryllate, both prepared with exclusion of CO₂, is filtered in the presence of KOH through an asbestos filter in a silver funnel. The filtrate is vacuum-evaporated in a nickel dish in the presence of H₂SO₄ and KOH. The first precipitate consists of Na₂CO₃ and some Be(OH)₂. As soon as the separation of the snow-white, shining sodium beryllate begins, the filtration is repeated and the solution further evaporated. The product is washed with alcohol and dried in a vacuum desiccator.

II. Monosodium beryllate and Be(OH)₂ exist as the solid-phase components in the system BeO-NaOH-H₂O at 30°C, when the concentrations of NaOH and BeOH are about 33% and 4.3%, respectively; at higher sodium hydroxide concentrations, monosodium beryllate is the only solid-phase component.

III. Sodium orthoberyllate with the formula Na₄BeO₃ is obtained as a white powder via the reaction of Na₂O with BeO in a silver boat at 500°C. For techniques of working with exclusion of CO₂ and atmospheric moisture, see Part I, the section on orthostannates and the original literature.

PROPERTIES:

Strongly hygroscopic crystals, decomposed by atmospheric CO₂.

REFERENCES:


Beryllium Sulfide

BeS

Beryllium sulfide may be prepared either by (I) synthesis from the elements, (II) reaction of the chloride with H₂S (which, however, does not yield chlorine-free material), or (III) from BeSO₄ or BeO. The last two methods should be used only when metallic Be is unavailable.

I.

Be + S = BeS

9.0 32.1 41.1

Sulfur vapor mixed with H₂ is passed over pure Be at a temperature of about 1150°C. The ground glass apparatus, shown in Fig.
254, consists essentially of a quartz tube with an enlargement at one end to serve as a sulfur receiver; the Be is contained in a boat made of quartz or, still better, of Al₂O₃ or BeO, and placed at the center of the quartz tube. To obtain a quantitative reaction, the product of the first run is finely pulverized in an agate mortar and again reacted with the sulfur vapor.

Von Wartenberg simplified the process as follows: a quartz tube of 15-mm. diameter and 700-mm. length, sealed at the lower end, is charged with 6 g. of Be and 30 g. of distilled S; the tube is slipped into a platinum-wound furnace, which is inclined at a 45° angle; the Be is first ground in a coffee mill and screened to give particles 0.2-0.5 mm. in diameter. The furnace is heated to 1350°C for about two hours; the sulfur evaporates constantly and flows back down the protruding portion of the tube, which acts as a reflux condenser. The sulfur vapor thus excludes air. After removal and cooling of the tube, its lower end is cut off and the easily removed, sintered cake is crushed and again treated with sulfur in the same fashion. The cut-off tube end may be resealed on a new tube section. After the cake is freed of sulfur under vacuum, it still contains Be flakes, which, however, can be separated by pulverizing and screening (0.1-mm. screen) to such an extent that the dirty yellow powder, which still retains a faint odor, no longer evolves \( \text{H}_2 \) when added to dilute acids. Analysis shows a BeS content of 98% on the basis of the determination of \( \text{H}_2\text{S} \) evolved; however, 2.4% of the product is insoluble in dilute \( \text{H}_2\text{SO}_4 \).

### II.

\[ \text{BeCl}_2 + \text{H}_2\text{S} = \text{BeS} + 2 \text{HCl} \]

79.9  34.1  41.1  72.9

Beryllium chloride, obtained by passing HCl over a red-hot mixture of BeO + C, is purified as thoroughly as possible by repeated sublimation in a quartz tube. Without opening the apparatus, the BeCl₂ is reacted with pure \( \text{H}_2\text{S} \) (prepared from S and \( \text{H}_2 \)). Too rapid sublimation of the BeCl₂ (at about 400°C) must be avoided by
increasing the temperature only very gradually if a satisfactory yield is to be obtained. Furthermore, the reaction must be localized by means of a water-cooled quartz tube, which is inserted in the quartz reaction tube. The chloride should be sublimed in the \( \text{H}_2\text{S} \) stream back and forth several times. The product, which still has a high chlorine content, is heated at 850 to 950\(^\circ\) in the \( \text{H}_2\text{S} \) stream for an additional hour. This yields a grayish, amorphous sulfide which still contains traces of chloride and which is less stable in air than the product made by method I.

III. Other preparative methods are the dry reduction of \( \text{BeSO}_4 \) with agents containing no hydrogen, e.g., \( \text{S} \) vapor, \( \text{CO} \), \( \text{CaC}_2 \), \( \text{Zn} \) or \( \text{Al} \). The best yields are obtained with \( \text{Al} \) (97\%, based on \( \text{BeSO}_4 \)). The reduction begins at 560\(^\circ\)C.

Beryllium sulfide may also be obtained by reaction of \( \text{CS}_2 \) with \( \text{BeO} \) at temperatures above 1200\(^\circ\)C.

**PROPERTIES:**

Gray to white powder with a faint odor of \( \text{H}_2\text{S} \) when exposed to air. Crystallizes in structure type B3 (ZnS). \( d \) 2.36.

**REFERENCES:**


**Beryllium Selenide and Beryllium Telluride**

\( \text{BeSe, BeTe} \)

\[ \text{BeSe} \]

\[ \text{Be} + \text{Se} = \text{BeSe} \]

9.0 79.0 88.0

Beryllium selenide is prepared from the elements in a \( \text{H}_2 \) stream at 1100\(^\circ\)C. Pure \( \text{Se} \) and pure pulverized \( \text{Be} \) are placed in a quartz reaction tube in separate boats made of \( \text{Al}_2\text{O} \) or \( \text{BeO} \), (or at least of quartz). The hydrogen should pass first over the heated \( \text{Se} \) and then, when laden with its vapor, over the \( \text{Be} \). A wash bottle filled with lead acetate is mounted at the exit end of the reaction tube to absorb the very toxic \( \text{H}_2\text{Se} \) present in the discharged gas. The \( \text{Se} \) is heated with a Bunsen burner; the uniform heat of an electric furnace is required for the \( \text{Be} \). The \( \text{BeSe} \) so obtained often shows a tendency to crystallize in long needles.
BeTe

Beryllium telluride can be prepared from the elements by the same method.

\[
\text{Be} + \text{Te} = \text{BeTe}
\]

\[
\begin{array}{ccc}
9.0 & 127.6 & 136.6 \\
\end{array}
\]

**PROPERTIES:**

Gray powders, decomposing relatively rapidly in air. Crystallize in structure type B3 (ZnS type). \(d\) (BeSe) 4.32, \(d\) (BeTe) 5.09.

**REFERENCE:**

Private communication from E. Tiede.

**Beryllium Nitride**

\[
\text{Be}_3\text{N}_2
\]

\[
3\text{Be} + 2\text{NH}_3 = \text{Be}_3\text{N}_2 + 3\text{H}_2
\]

\[
\begin{array}{ccc}
27.1 & 34.1 & 55.1 \\
\end{array}
\]

Instead of synthesizing the nitride from the elements, it may be obtained more easily and in higher yield by heating metallic Be in an \(\text{NH}_3\) stream.

The commercial metal is crushed in a steel mortar and screened through a 100-mesh (per inch) sieve; the powder is placed in a corundum boat, which is heated in a porcelain tube in a dry \(\text{NH}_3\) stream at 850°C for three hours. The reaction product is then pulverized in an agate mortar and heated in the \(\text{NH}_3\) stream at 1000°C; this procedure is repeated three times. The product so obtained usually contains only 94-95% \(\text{Be}_3\text{N}_2\). A purer product might be obtained by the use of metal distilled in high vacuum and by careful manipulation.

**PROPERTIES:**

Gray-white powder; stable in air; decomposes rather slowly on contact with boiling acids. Crystallizes in structure type \(\text{D5}_3\) (C sesquioxide type).

**REFERENCES:**

Beryllium Azide

Be(N₃)₂

\[ \text{Be(CH}_3\text{)}_2 + 2\text{HN}_3 = \text{Be(N}_3\text{)}_2 + 2\text{CH}_4 \]

Pure dimethylberyllium is sublimed into a reaction vessel cooled with liquid N₂; then an absolutely dry ether solution of excess HN₃ is condensed on top of the dimethylberyllium layer. As the reaction mixture thaws, a vigorous reaction with evolution of methane starts even before all of the ether is melted (m.p. −116°C), and Be(N₃)₂ separates out as a white precipitate. The ether and excess HN₃ are then distilled off under high vacuum.

PROPERTIES:

White, solid substance; explosive in the presence of a flame; insensitive to shock. Rapidly decomposed in moist air. Hydrolyzes in aqueous solution to such an extent that the substance may not be recovered undecomposed even when the solvent is very carefully distilled off in a high vacuum.

REFERENCE:


Beryllium Carbides

Be₂C; BeC₂

Be₂C

I. \[ 2\text{Be} + \text{C} = \text{Be}_2\text{C} \]

| 18.0 | 12.0 | 30.1 |

A mixture of metallic Be (turnings or powder) and finely divided graphite or calcined acetylene black is reacted at 1700°C for 20 to 30 minutes. The yield is 85%.

II. \[ 2\text{BeO} + 2\text{C} = \text{Be}_2\text{C} + 2\text{CO} \]

| 50.0 | 36.0 | 30.0 | 56.0 |

A blend of calcined BeO and half its weight of carbon made from sugar is mixed with 5% of starch and 15% of water, compressed into cylinders, dried, calcined, and finally heated in H₂ at two
atmospheres gauge and 1930°C for 10 to 15 minutes; an 85-92% pure product is obtained as beautiful, brick-red crystals. The reaction does not start below 1700°C, but the carbide decomposes extensively above 2200°C. For this reason, the more convenient electric arc furnace process is not recommended. According to Messerknecht and Biltz, the simplest form of the arc process apparatus consists of a graphite crucible with a carbon electrode immersed in the reactant mixture (110v., 30 amp.).

Low concentration products may be enriched by treatment with hot dilute hydrochloric acid (however, a portion of the carbide is lost by decomposition). The excess C may thus be decanted and the BeO dissolved. In this manner, an enrichment to more than 95% Be$_2$C is possible; in this manner, an enrichment to more than 95% Be$_2$C is possible; the balance is BeO and free C.

PROPERTIES:

Yellow-red, finely crystalline powder, slowly decomposing in moist air. Crystallizes in structure type Cl (antifluorite type).

REFERENCES:


BeC$_2$

Be + C$_2$H$_2$ $\rightarrow$ BeC$_2$ + H$_2$

According to Durand, BeC$_2$ is formed by passing dry acetylene at 450°C over Be powder in a Pyrex tube. The product appears black due to free C formed via thermal decomposition of the acetylene.

PROPERTIES:

Generates acetylene with H$_2$O and (moderately) with dilute HCl.

REFERENCE:

17. ALKALINE EARTH METALS

Beryllium Acetate

Be(CH_3COO)_2

Be_4O(CH_3COO)_6 + 2 CH_3CO · Cl + 2 CH_3COOH
406.3  157.0  120.1
= 4 Be(CH_3COO)_2 + 2 HCl + (CH_3CO)_2O
508.4  72.9  102.1

Basic beryllium acetate (4 g.) is dissolved in 50 ml. of boiling glacial acetic acid and refluxed with 4-5 g. of acetyl chloride for a short time. The precipitate of Be(CH_3COO)_2 forming after a few minutes is filtered off, washed with glacial acetic acid and with cold chloroform, and dried in a vacuum desiccator. The yield is 90-94%.

PROPERTIES:

Stable for several weeks in a closed vessel at room temperature. Slowly splits off acetic anhydride (rapidly when heated) and is converted to basic beryllium acetate, which sublimes. Undergos partial decomposition to acetic anhydride and beryllium oxide when heated rapidly.

Barely attacked by cold water, is hydrated at elevated temperature. Insoluble in all solvents for basic beryllium acetate.

REFERENCE:


Basic Beryllium Acetate

Be_4O(CH_3COO)_6

I. Basic beryllium carbonate (40 g.) is mixed with 80 ml. of glacial acetic acid and stirred, with heating, until CO_2 evolution ceases. The end of the reaction is also recognized by the start of precipitation of white, semitranslucent crystals; otherwise, there is an amorphous, white residue. The solution is cooled to room temperature and the crystallized basic acetate is filtered off and dried in air.

The crude product is treated with 60-80 ml. of chloroform, and any insoluble residue is removed by filtration. The basic salt, which crystallizes in colorless octahedra, is filtered off and freed of residual chloroform in a vacuum desiccator. The product melts at 284°C and sublimes without a residue at reduced pressure. The yield is 28 g.
II. A method described by Hardt avoids contamination of the product by ammonium salts and solvent occlusions and makes purification by sublimation unnecessary.

Beryllium hydroxide or basic beryllium carbonate is stirred with glacial acetic acid to a paste and evaporated to dryness in a laboratory oven at 120 to 130°C. The crude product thus formed is extracted with glacial acetic acid in a Soxhlet apparatus (using a glass wool filter); after cooling, it crystallizes from the extract in well-formed octahedra, which are filtered off and dried at 130°C.

This is followed by a second Soxhlet extraction with \( \text{CCl}_4 \), since the ammonium salts from the starting material still remain undissolved. The product is analytically pure after drying at 100°C.

**PROPERTIES:**

At room temperature the molecular lattice is of the space group \( T_\text{m}^4(\alpha) \). Transition to other modifications (\( \gamma, \beta \)) occurs at 150 to 155°C. Very soluble in chloroform; readily soluble in boiling benzene, toluene, xylene, Tetralin and glacial acetic acid; less soluble in \( \text{CCl}_4 \), acetic anhydride and acetyl chloride; sparingly soluble (0.3%) in diethyl ether.

In anhydrous boiling methanol following initial dissolution, splits off acetic anhydride with formation of highly aggregated basic acetates.

Quite stable in cold water, but is rapidly hydrolyzed in hot water.

Begins to sublime at about 200°C, softens at about 280°C to a nematic or smectic (liquid crystal) state and melts at 183 to 184°C with sublimation. May be distilled at 1-2 atmospheres gauge. Pure basic beryllium acetate leaves a residue of 0.3-0.5% BeO after sublimation.

For the preparation of basic beryllium formate and basic beryllium propionate, see the literature cited under II; also H. Hendus and H. D. Hardt, Z. anorg. allg. Chem. 277, 127 (1954).

**REFERENCES:**

Magnesium

Generally, very pure magnesium is prepared by refining commercial magnesium via distillation or, still better, by sublimation in high vacuum.

Magnesium is usually made commercially by electrolysis of molten, dehydrated carnallite (MgCl$_2$·KCl), with an Acheson graphite anode and an iron cathode.

The crude metal obtained by electrolysis contains up to 2.7% Cl, besides other impurities (Fe, Al, Si, N). Purification is effected by melting with fluxing agents or, better, by repeated filtration. This may be done simply by pushing a sheet iron screen downward through the melt. This reduces the chlorine content considerably (final content: 0.003% Cl).

Another method of purification consists in refining with Zr. Addition of 2-4% of ZrCl$_4$ to Mg melts results in precipitation of Fe, Al, Si and Mn but not of Cu. The Zr can be removed by subsequent passage of H$_2$, still retaining the degree of purity previously achieved. Magnesium thus prepared is highly resistant to corrosion.

Pure magnesium (99.9%), absolutely free of halogen, is obtained by the Radentheiner process.

I. SUBLIMATION OF THE CRUDE METAL

In the laboratory, the following simplified method may be used: the sublimation vessel shown in Fig. 255 (see also the apparatus described for the distillation of Ca) consists of an iron tube (60-mm. diameter and 500 mm. long), which is closed at one end and has a threaded vacuum-tight lid on the other. The lid is fitted with a nipple for connection to a high-vacuum system. The lower end of this retort contains an iron tube with the crude magnesium; the open end of the tube is preferably closed by one or two fine-mesh wire screens which are clamped to the tube. The conical iron tube is inserted into the colder zone of the sublimation vessel. The tube consists of two halves held together by rings (see Fig. 255). Before the preparation, the interior walls of the tube are dusted with MgO in order to prevent sticking of the condensate.

The sublimation temperature is stated in the literature to be about 600°C at a vacuum of 10$^{-3}$ mm. If the condensing surface is at 400 to 500°C, the crystals will be dendritic; larger quantities agglomerate to massive blocks. At higher temperatures (600°C), large single crystals are formed.
The metal obtained after a single sublimation contains Fe, Al, Si and Cl in amounts less than 0.001%. After repeated sublimation the impurities cannot be identified either chemically or spectroscopically. The sublimed metal can be remelted in an argon atmosphere at 300-400 mm.

![Diagram of purification process](image)

**Fig. 255. Purification of magnesium by sublimation.**

II. When larger quantities (about 1 kg.) must be sublimed in a single operation, the metal is condensed in an apparatus of larger capacity, using a water-cooled cylinder.

**PROPERTIES:**


Cold water reacts only slowly with magnesium; the reaction is much more rapid in boiling water. The metal dissolves violently in acids.

**REFERENCES:**

K. E. Mann, Z. Metallkunde 44, 264 (1953).
I. W. Kaufmann and P. Siedler, Z. Elektrochem. 37, 492 (1931).
II. I. Hérenguel and G. Chaudron, Comptes Rendus Hebd. Séances Acad. Sci. 193, 771 (1931); 195, 1272 (1932); see also G. Chaudron in A. E. van Arkel, Reine Metalle [Pure Metals], Berlin 1939, p. 111.
**Magnesium Hydride**

\[ \text{MgH}_2 \]

I.  
\[ \text{Mg} + \text{H}_2 = \text{MgH}_2 \]

24.3 22.4 26.3

Magnesium and hydrogen react at 570°C and 200 atmospheres in the presence of \( \text{MgI}_2 \) as a hydrogen transfer agent to form \( \text{MgH}_2 \). The yield is 60%.

II. Magnesium hydride is formed when magnesium dialkyls (diethyl, dibutyl, diphenyl) or the corresponding Grignard compounds are heated to 175–200°C under high vacuum for several hours.

**PROPERTIES:**

White, water-sensitive solid; not spontaneously combustible. Insoluble in ether; nonvolatile; stable to 280°C under vacuum.

**REFERENCES:**


**Magnesium Chloride**

\[ \text{MgCl}_2 \]

**ANHYDROUS MgCl\(_2\)**

In the method developed by Richards, \( \text{MgCl}_2 \) is prepared from a mixture of \( \text{NH}_4\text{Cl} + \text{MgCl}_2 \cdot 6\text{H}_2\text{O} \) or from the double salt \( \text{NH}_4\text{Cl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O} \) by dehydration in a HCl stream. The reaction of \( \text{MgO} \) with a gas mixture of CO and Cl\(_2\) is much better suited for the preparation of larger quantities (more than 100 g.).

I.  
\[ \text{NH}_4\text{Cl} + \text{MgCl}_2 \cdot 6\text{H}_2\text{O} \]

256.8 95.2 53.5 108.1

Equimolar quantities of \( \text{MgCl}_2 \cdot 6\text{H}_2\text{O} \) and \( \text{NH}_4\text{Cl} \) are crystallized from aqueous solution somewhat above 50°C. After separating
the mother liquor at this temperature the salt is recrystallized once, slightly predried and filled while still hot into a quartz boat, which is then inserted into a quartz tube. Dehydration in a dry HCl stream proceeds first at 100°C for three hours (avoid melting of the hydrated crystals), then at 250°C for one hour, and finally at 400°C for one hour. Finally, the product is quickly melted and freed of HCl while cooling in a stream of CO₂. The salt thus prepared contains about 0.1% MgO and 0.05% SiO₂; it may be stored over P₂O₅.

If high purity is not required, it will suffice to start with a mixture of NH₄Cl and MgCl₂·6H₂O.

The consumption of HCl may be reduced substantially through dehydration of the hexahydrate or of ammonium carnallite by heating at 200°C under vacuum or by storage in a desiccator over P₂O₅. The drying with HCl may then be started directly at 200°C.

Even though HCl begins to split off at 106°C when the hexahydrate is heated in air, it is possible to dry the material at 150°C without formation of undesirable amounts of basic salt, provided the evaporation is rapid. It is advisable to place the hexahydrate in a large porcelain dish covered with a wide funnel, which serves as a partial condenser of the hydrochloric acid vapors formed. Thus, the formation of the basic salt is reduced to a minimum. The dihydrate begins to crystallize at 180°C. At this point the melt is poured onto an aluminum sheet and crushed while still warm. This product still contains 2.3-2.8 moles of water per mole of MgCl₂.

According to Treadwell, the HCl may be recycled after drying with concentrated H₂SO₄, but this requires elaborate equipment; besides, traces of chlorosulfonic acid formed react with MgCl₂ to yield MgSO₄.

$$\text{MgO} + \text{Cl}_2 + \text{CO} \rightarrow \text{MgCl}_2 + \text{CO}_2$$

Magnesium oxide can be chlorinated quantitatively only in the presence of a reducing agent (CO). The reaction depends critically on the thermal pretreatment of the MgO; magnesium carbonate calcined at 800°C is still very reactive. Commercial CO in cylinders is not suitable, since the H₂ it contains forms water, which damages the apparatus; for this application CO is prepared in a small generator.

a. Carbon monoxide generator. The reactor is a vertically mounted quartz tube with an I.D. of 20 mm. and length of 600 mm., which is maintained at about 950°C. A somewhat narrower, sealed-off quartz tube is pushed into the lower hot zone; this tube serves as a retaining grating. The reactor is charged
with dry activated carbon of 5-mm. particle size and may be refilled through a side arm sealed on at the upper end. To start the reaction, CO$_2$ from a cylinder is added from the top. A small CO flame is allowed to burn at a capillary branching off from the outlet tube to provide a simple test for the CO content of the generated gas. The outlet gas passes through a pressure relief valve and a bubble counter and is then mixed with Cl$_2$, which is metered by the same method.

b. Magnesium oxide furnace. The reaction vessel is a vertically mounted, 700-mm.-long quartz tube with an I.D. of 35 mm. In the lower portion there is a 4-mm.-diameter, funnel-shaped, centered drip nozzle filled with a layer of quartz fragments to support a charge of 500 g. of MgO. The gas flow rate is 400 ml./min. (200 ml. Cl$_2$ + 200 ml. CO), and the reaction temperature is 750°C. The exit gas has a 1% excess of CO and this ensures that the Cl$_2$ content is kept below 3 · 10$^{-5}$%. The gases flow upward, countercurrent to the salt, which drips down. The salt drops emerging from the nozzle should fall free into the receiver which is mounted underneath by means of a ground glass joint. The pure white, brittle rods and grains of MgCl$_2$ may be easily removed later. However, the entire oxide charge must be wetted with molten chloride before the first drops appear. This occurs only 2–3 hours after the start of the chlorination.

The exit gases from the top of the reactor pass a small dust collector, which retains, aside from the dust, the impurities of the oxide. The gases are then vented. Through a capillary branching off the gas discharge line, a small gas stream may be diverted to a Bunsen flame containing a glowing copper wire. In this way one may test the gas composition. The desired excess of CO can be recognized by a faintly blue cast; traces of Cl give a green copper flame (Beilstein test).

PROPERTIES:

Leafy crystalline mass. Melts at 712°C to a water-clear, mobile liquid. May be distilled at bright red heat in a H$_2$ stream. d 2.41. More hygroscopic than the chlorides of the higher alkaline earth metals. Liberates Cl$_2$ when heated to 300°C forming oxides and oxychlorides.

REFERENCE:

MgCl₂ · 6 H₂O

Very pure material may be prepared from 500 g. of commercial MgCl₂ · 6 H₂O, which is dissolved in water. The solution is saturated with H₂S, some ammonia is added, and the solution is kept warm for several days. The supernatant solution is decanted and Ca is precipitated from it by the addition of a small amount of very pure ammonium oxalate. After settling, the decanting is repeated. The filtrate is tested for completion of the reaction by repeated addition of oxalate, followed by long settling.

The clear solution is evaporated and the salt is calcined. The mixture of MgO and oxychloride thus obtained is washed on a filter for 60 hours with distilled water until the wash water no longer contains any Na and K. Nevertheless, the Mg salt redissolved in pure distilled hydrochloric acid may not be free of these metals; the procedure described above must then be repeated until no further traces of Na and K can be detected.

On concentration, the MgCl₂ · 6 H₂O precipitates from the aqueous solution between -3 and +116°C.

Quartz should be used if no platinum equipment is available. It is advisable to use electric heating to avoid contamination by the gases of the flame (sulfur).

**PROPERTIES:**

The hexahydrate forms bitter, deliquescent, monoclinic crystals. d 1.56.

AMMONIUM CARNALLITE

The ammonium chloride required for the preparation of the double salt is treated with nitric acid to break down any amines and is then dried and sublimed several times. It is then recrystallized 5 to 6 times, and finally repeatedly sublimed in a stream of pure air (which is washed with concentrated K₂CO₃ and concentrated H₂SO₄).

The pure double salt is crystallized from a mixture of one mole of MgCl₂ · 6 H₂O in 30 ml. of water and one mole of NH₄Cl in 70 ml. of water above 50°C (preferably after boiling for a few minutes).

**REFERENCES:**


**Magnesium Bromide**

MgBr₂

Magnesium bromide can be obtained by dehydration of the hexahydrate in a stream of HBr (I) or via the reaction of Br₂ with Mg in anhydrous diethyl ether (II).

I. 

\[
\text{MgCl}_2 \cdot 6 \text{H}_2\text{O} \rightarrow \text{MgBr}_2 \cdot 6 \text{H}_2\text{O} \rightarrow \text{MgBr}_2 \\
203.3 \quad 292.2 \quad 184.1
\]

The hydroxide is precipitated with ammonia from MgCl₂ solution. It is then washed until the dissolved sample is halogen-free, suspended in water, and dissolved by the introduction of HBr gas. The salt obtained by concentrating the solution is recrystallized and dehydrated in a stream of HBr. Traces of HBr are removed by heating in dry, oxygen-free N₂.

If higher purity material is desired, quartz equipment must be used. Ground glass joint apparatus prevents contact of the salt with the atmosphere. The procedure follows the Baxter method for the preparation of alkaline earth halides.

II. 

\[
\text{Mg} + \text{Br}_2 = \text{MgBr}_2 \\
24.3 \quad 159.8 \quad 184.1
\]

Pure Br₂ is evaporated at 50 to 55°C in a wash bottle and carried by a stream of dry N₂ (15 ml./minute) to the bottom of a round, 500-ml. flask. The flask contains 150 ml. of freshly distilled, anhydrous ether and 10 g. of clean Mg turnings. It is equipped with a high-speed stirrer and a CaCl₂ tube on the gas outlet tube (to exclude atmospheric moisture). Externally the flask is cooled to below room temperature to remove the considerable heat of reaction.

The reaction is stopped when 15 ml. of Br₂ has evaporated. The liquid is decanted into a dry flask and crystallization of the MgBr₂ trietherate is initiated by cooling below 0°C. The mother liquor is discarded. The crystals are immediately treated with anhydrous benzene and allowed to stand at room temperature. The ether-benzene mixture dissolves most of the impurities, while MgBr₂ is only slightly soluble in it. The suspension is then again cooled to 0°C; the crystals are rapidly filtered off and washed.
with cold (0°C) benzene. The ether is removed by a water jet aspirator and the etherate is decomposed by raising the temperature to 150-175°C over a period of a few hours. Oil-pump vacuum is applied for one hour to remove residual ether. The yield of MgBr₂ is 60-70%. The salt is 99.3-99.6% pure; without the benzene purification step, the purity is only 90-95%.

**PROPERTIES:**

Pure white salt. M.p. 711°C; d 3.72. Crystallizes in structure type C6. Very hygroscopic. The melt is decomposed by atmospheric oxygen and turns yellow, forming MgO and Br₂.

**PROPERTIES:**


**Magnesium Iodide**

\[ \text{MgI}_2 \]

Magnesium iodide can be prepared either by dehydration of its hydrate in an HI stream (I), from the elements (II), or via the reaction of I₂ and Mg in anhydrous ether (III).

I. \[ \text{MgI}_2 \cdot 8 \text{H}_2\text{O} \rightarrow \text{MgI}_2 \]

\[ 422.3 \rightarrow 278.2 \]

The method is analogous to method (I) for MgBr₂.

II. \[ \text{Mg} + \text{I}_2 = \text{MgI}_2 \]

\[ 24.3 \rightarrow 278.2 \]

Clean Mg turnings (0.5 g.) are heated to 600°C in a porcelain boat located in the center of a Vycor tube. The tube is evacuated and 5-6 g. of I₂ is placed at one end. The I₂ is sublimed repeatedly from one end of the tube to the other, thus passing over the Mg. Finally, the center only of the tube is heated. The I₂ then collects at the cold ends of the tube, while some Mg remains in the boat. The pure, white MgI₂ platelets deposit on either side of the boat. The tube must be cut open to remove the sublimate.
III. Anhydrous MgI$_2$ can also be obtained by decomposing the etherate under high vacuum at 230°C; the etherate may be prepared in the same way as described for MgBr$_2$ (Method II). The method does not seem to offer any special advantage.

**PROPERTIES:**

Hexagonal platelets. M.p. in hydrogen 650°C; d 4.43. Crystallizes in structure type C6 (layer lattice). Extremely hygroscopic. At room temperature, crystals of the octahydrate precipitate from aqueous solution; the hexahydrate is stable above 34°C.

**REFERENCES:**


**Magnesium Oxide**

MgO

Magnesium oxide is generally obtained by calcining easily decomposed magnesium compounds such as the hydroxide, the nitrate, the oxalate and other salts of organic acids. However, the principal raw material is the carbonate (the sulfate may also be converted to the oxide at high temperatures).

Basic magnesium carbonate is solidly packed into the lower half of a tall porcelain crucible. An electric crucible furnace is slowly heated. All the CO$_2$ is removed within about one hour at 600°C. The still hot crucible is rapidly cooled over P$_2$O$_5$ in a desiccator. The MgO is obtained as a loose, white mass which is readily soluble in dilute hydrochloric acid.

**PROPERTIES:**

Formula weight 40.32. M.p. 2642°C, b.p. 2800°C. Crystallizes in structure type B1; d 3.58. The physical properties and the chemical reactivity depend to a large extent on the method of preparation (starting material, calcining temperature, time).

**REFERENCES:**

Private Communication from E. Tiede.
Magnesium Hydroxide

Mg(OH)$_2$

Magnesium hydroxide may be precipitated with alkali from solutions of magnesium salts. It may also be obtained by hydration of magnesium oxide and by the reaction of water with magnesium amalgams.

I. MICROCRYSTALLINE Mg(OH)$_2$:

\[
\text{MgCl}_2 \cdot 6 \text{H}_2\text{O} + 2 \text{NH}_4\text{OH} = \text{Mg(OH)}_2 + 2 \text{NH}_4\text{Cl} + 6 \text{H}_2\text{O}
\]

A solution of MgCl$_2 \cdot 6$ H$_2$O, almost saturated at room temperature, is treated with a large excess of concentrated ammonium hydroxide at 70°C, while high-speed agitation is maintained. Since Mg(OH)$_2$ is very sensitive to CO$_2$, the distilled water employed must be thoroughly boiled before use. The ammonia used for the precipitation is prepared by passing NH$_3$ gas, from which CO$_2$ has been carefully removed with solid KOH, into CO$_2$-free water. Because of the sensitivity of Mg(OH)$_2$ to silicic acid, only Pyrex glass vessels should be used.

After the precipitation, the material should remain submerged under the mother liquor for two days. During this time it is re-heated to 70°C several times. The precipitate is purified first by washing with CO$_2$-free water, then by centrifuging in paraffin-coated nickel tubes. Precipitation and washing are carried out in the apparatus shown in Fig. 256, which is self-explanatory. The substance is dried under vacuum, first over solid KOH and then over P$_2$O$_5$.

Fig. 256. Preparation of magnesium hydroxide.
The impurities in the material thus prepared are approximately: < 0.1% Cl, 0.27% CO₂, 0.01% SiO₂. Loss on calcining (1000°C) 31.36% (theoretical: 30.88%).

II. MACROCRYSTALLINE Mg(OH)₂:

\[ \text{MgCl}_2 \cdot 6\text{H}_2\text{O} + 2\text{KOH} = \text{Mg(OH)}_2 + 2\text{KCl} + 6\text{H}_2\text{O} \]

A wide-neck Pt vessel is charged with 1375 g. of KOH, 48.5 g. of \( \text{MgCl}_2 \cdot 6\text{H}_2\text{O} \) and 243 ml. of water. This mixture is heated in an electric furnace to 210°C and held at this temperature until the melt becomes clear (about 30 minutes). It is then allowed to cool to room temperature over a period of 18 hours. The solidified melt is dissolved in water and the solution filtered through a glass frit. The crystals remaining on the filter are washed several times with distilled water and dried at 100°C for two hours. The well-shaped crystals have a diameter of about 0.2 mm; they are free of CO₂ and contain about 0.15% K.

**PROPERTIES:**

d 2.4. Crystallizes in structure type C6. Readily soluble in acids. Thermal degradation to MgO begins at temperatures above 200°C under vacuum.

**REFERENCES:**

I. R. Fricke, R. Schnabel and K. Beck, Z. Elektrochem. 42, 881 (1936); for other preparative methods, see there, as well as R. Fricke et al., Z. Elektrochem. 41, 174 (1935); Z. anorg. allg. Chem. 166, 255 (1927).


**Magnesium Sulfide**

\( \text{MgS} \)

The synthesis of MgS from its elements is impractical since the reaction can be very violent. Heating of the metal in a stream of \( \text{H}_2\text{S} \) is more adaptable to the laboratory. Very pure MgS is formed in the reaction of \( \text{CS}_2 \) with \( \text{MgSO}_4 \) at 900°C. If one prefers not to use an oxygen-containing compound as a starting material, ammonium magnesium chloride may be reacted in a stream of \( \text{H}_2\text{S} \).
I.  \[ \text{Mg} + \text{H}_2\text{S} = \text{MgS} + \text{H}_2 \]

A stream of dry \( \text{H}_2\text{S} \) is passed over \( \text{Mg} \) turnings placed in a graphite boat or, better, in a boat made of sintered magnesia (\( \text{H}_2\text{S} \) flow rate 8 ml./min.). The reaction starts at 580°C, and once started, may be continued at lower temperature and higher flow rate (15 ml./min.). Unreacted \( \text{Mg} \) is distilled off by heating to 800°C under high vacuum. The pure white product contains 99.5% \( \text{MgS} \); it reacts vigorously with water at room temperature.

II.  \[ 3\text{MgSO}_4 + 4\text{CS}_2 = 3\text{MgS} + 4\text{COS} + 4\text{SO}_2 \]

The Von Wartenberg modification of the \( \text{CS}_2 \) process of Tiede and Richter proceeds as follows: about 20 g. of finely pulverized \( \text{MgSO}_4 \) (evaporated with a small excess of \( \text{H}_2\text{SO}_4 \)) is placed in a quartz tube just before all of the \( \text{H}_2\text{SO}_4 \) has been removed. The sulfate is heated in pure \( \text{N}_2 \) for half an hour at 700°C and then in \( \text{N}_2 \) saturated with \( \text{CS}_2 \) vapor for ten hours at 750°C. At this point, the iodine solution test should show no further \( \text{SO}_2 \) in the exit gas. The reaction temperature cannot be raised since elemental \( \text{C} \) begins to separate from the gas at 800°C. The very pure, loose product thus obtained is completely white.

III.  \[ \text{NH}_4\text{Cl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O} + \text{H}_2\text{S} = \text{MgS} + 2\text{HCl} + \text{NH}_4\text{Cl} + 6\text{H}_2\text{O} \]

In the Banks modification of the Sarge method, the reaction temperature must be held below the melting point of \( \text{MgCl}_2 \) for about one hour while \( \text{H}_2\text{S} \) is passed over ammonium carnallite. It is then gradually (90 minutes) raised to 1000°C. The product is a white to cream-colored powder, which is very pure except for traces of chloride.

PROPERTIES:

- White powder. M.p. > 2000°C; d 2.86. Crystallizes in structure type B1. Crystalline \( \text{MgS} \) is only slowly attacked by water; it is completely soluble in dilute \( \text{HCl} \).

REFERENCE:


17. ALKALINE EARTH METALS

Magnesium Selenide
MgSe

The preparation of MgSe is analogous to that of BeSe:

\[
\text{Mg} + \text{Se} = \text{MgSe}
\]

24.3 79.0 103.3

The optimal reaction temperature is 750°C (see also MgTe below).

PROPERTIES:

Slightly gray powder; decomposes very rapidly in air. Crystallizes in structure type B1. \(d\) 4.21.

REFERENCES:

Private communication from E. Tiede.

Magnesium Telluride
MgTe

The direct preparation from the elements proceeds very violently at elevated temperature; it can be controlled by reacting only small quantities at a time.

Commercial Mg of at least 99.8% purity is used; the tellurium must be purified in most cases because of its selenium content. Twice recrystallized basic tellurium nitrate is freed of nitric acid by boiling in concentrated \(\text{H}_2\text{SO}_4\), and then HCl gas is passed through the boiling solution for several hours. Finally, the solution is diluted and the Te is precipitated with hydrazine. The Te, still containing some oxide, is distilled under vacuum.

The apparatus for the synthesis of MgTe consists of a tube with male ground joints at both ends. The tube is fitted with a side arm into which a small funnel can be inserted; the funnel may be closed by means of a glass rod. A small amount of a fine mixture of Mg powder and Te (atomic ratio 1:1.1 to 1:1.2) is added to the funnel and, by lifting the glass rod, dropped into a boat made of corundum or preferably, of carbon (MgO may also be suitable). A hydrogen flow is maintained over the boat during the filling. The boat is then pushed sideways and the contents made to react by fanning with a small flame. This operation is repeated until a sufficient amount has accumulated. A small electric oven is then placed over the
reactor tube, one end and the side arm are closed with ground-glass caps, and the other end is connected to a high-vacuum system. The substance is then heated under high vacuum at 600 to 700°C for a long time in order to distill off excess tellurium. After the completion of this heat treatment, the cooled product is bottled under highly purified nitrogen.

PROPERTIES:

Pure white powder. Decomposes in damp air, forming H₂Te, which then oxidizes to Te and appears on the surface of the telluride as a black deposit. d 3.85. Crystallizes in structure type B₄ (wurtzite type).

REFERENCE:


Magnesium Nitride

Mg₃N₂

Finely divided Mg reacts with nitrogen at elevated temperatures. The nitrogen must be very pure in order to obtain oxide-free nitride. For this reason, using a dry NH₃ stream, instead of the N₂, is advisable.

Magnesium filings are placed in a boat made of porcelain or, preferably, of sintered magnesia and inserted into a porcelain tube. This tube is connected by means of a tee with a source of N₂ and an apparatus for generating dry NH₃. The other end of the porcelain tube is connected to a U tube filled with equal volumes of CaO and KOH pellets. The exit gases are passed through an absorption unit consisting of two Erlenmeyer flasks filled with dilute H₂SO₄. The inlet tube of the first flask does not dip into the liquid.

After the air is completely displaced from the apparatus by the NH₃ (air bubbles cease to emerge from the second Erlenmeyer flask), the Mg is heated at 800 to 850°C for four hours. The onset of nitride formation is recognized by incandescence of the Mg and the evolution of H₂. A high NH₃ flow must be maintained at the peak of the reaction to avoid sucking the absorption fluid into the reactor. Since the finished material always contains adsorbed NH₃, heating in a N₂ stream should be continued at the same temperature for 90 minutes. Because of the high moisture sensitivity of the material, bottling must be carried out with the usual precautions.

PROPERTIES:

Loose powder, green-yellow to yellow-orange; d 271. Crystallizes in structure type D₅₃ (carbon sesquioxide type). Very
sensitive to moisture; decomposes rapidly in air to Mg(OH)$_2$ and NH$_3$.

REFERENCES:

M. von Stackelberg and R. Paulus, Z. phys. Chem. (B) 22, 305 (1933); see also H. Grubitsch, Anorganisch-präparative Chemie [Inorganic Preparative Chemistry], Vienna, 1950, p. 306.

**Magnesium Azide**

\[ \text{Mg(N}_3\text{)}_2 \]

The preparation is analogous to that described for beryllium azide (p. 899), using diethylmagnesium in ether-dioxane. The reaction starts on thawing below 0°C.

PROPERTIES:

White substance, sensitive to moisture, insoluble in ether and in tetrahydrofuran. Slightly explosive on contact with a flame. Only the basic azide is recovered from aqueous solutions when the water is distilled off under high vacuum.

REFERENCE:


**Magnesium Phosphide and Magnesium Arsenide**

\[ 3 \text{Mg} + 2 \text{P} = \text{Mg}_3\text{P}_2 \quad 3 \text{Mg} + 2 \text{As} = \text{Mg}_3\text{As}_2 \]

I. In the method of Zintl and Husemann, a H$_2$ stream laden with vapors of P or As is passed over heated pulverized magnesium.

The substances may be prepared in the apparatus shown in Fig. 257 without coming into contact with air. Here \( S_1 \) and \( S_2 \) are two Vycor boats; \( S_1 \) is filled with 5 g. of purified red P (or 12 g. of sublimed As); \( S_2 \) is filled with 4 g. of Mg powder, prepared from pure metal with a milling machine in the absence of air. After thorough evacuation, pure H$_2$ is introduced at \( \mathcal{H} \) and escapes at \( \mathcal{A} \). Boats \( S_1 \) and \( S_2 \) are separately heated with two electric furnaces \( \mathcal{O}_1 \) and
The initial temperature is 600°C in both furnaces. At the end of the reaction, the product in \( S_2 \) is kept at about 700°C for a short time in order to remove the excess of P (or As). The Vycor cylinder \( Z \), which is sealed at one end, prevents the back-diffusion of the P (or As) vapor.

This method yields the compounds in finely crystalline form; the \( \text{Mg}_3\text{P}_2 \) is bright yellow, the \( \text{Mg}_3\text{As}_2 \), intensely brown-red. The cylinder \( Z \) with the two boats is pushed toward \( B \) (against the \( \text{H}_2 \) flow) by means of a glass rod introduced at \( A \). Boat \( S_2 \) is then pulled to the left to \( C \) and overturned at that point so that the material accumulates at \( D \). Outlet \( A \) is then closed off and the compound is pulverized at \( D \) by means of a glass rod with a pestle-shaped end, which is introduced at \( E \). The distribution vessel \( V \) is then detached at \( F \) and is closed (under a hydrogen blanket) by a ground glass plug. A connection is then made at \( H \) to a flexible, corrugated tombac tube, which leads to the pump and the hydrogen generator. Rubber tubing is not suitable for this purpose because it gives off moisture. Finally, the powder is distributed into the thin-wall glass bulbs \( K \) and tubes \( M \) by tilting vessel \( V \). The bulbs and the tubes are melt-sealed. The samples in \( K \) are used for analysis; therefore the bulbs are weighed together with their ground joints before assembly and after sealing off. The material thus obtained is very pure.

![Fig. 257. Preparation of magnesium phosphide and magnesium arsenide.](image)

II. A porcelain boat 10 × 15 × 60 mm.—a boat made of \( \text{Al}_2\text{O}_3 \) or \( \text{MgO} \) is recommended for the metal—is filled with very fine Mg shavings turned from a solid metal block. A second boat is filled with 6 g. of purified red P (or 14 g. of sublimed As). Both boats are pushed to the closed end of a 500-mm. combustion tube which has a diameter just sufficient to accommodate the boats. The tube is closed with a rubber stopper fitted with a stopcock and evacuated.
by means of an oil pump while being gently fanned with a flame. Even better, the tube is drawn out using a torch, and a section 350 mm. long is sealed off under high vacuum.

After the metal has been heated to dull red heat, the P (or As) is heated with a second burner and distilled onto the Mg. The reaction of the two elements is accompanied by bright incandescence. In order to avoid removal of P (or As) from the reaction site while heating the Mg or during the reaction itself, the center portion of the reaction tube is heated by a short multiple-tube burner, so that little or no P or As condenses on the cold surface of the rubber stopper. This also assures that the stopper will be able to relieve any pressure buildup in the tube.

In order to remove excess P (or As) from the finished product, the tube is shifted so that only the two boats are heated by the multiple-tube burner. Heating is continued for 30 minutes. In the case of the arsenide, the excess nonmetal can sometimes be removed only after pulverizing the reaction product. After cooling, the tube is filled with dry Cl₂. The boat is taken out and the moisture-sensitive substance is sealed into a prepared ampoule as shown in Fig. 258.

Fig. 258. Bottling of magnesium phosphide under CO₂ blanket.

**PROPERTIES:**

The phosphide is bright yellow, the arsenide is brown-red. Stable in completely dry air at room temperature, decompose in moist air (Mg₃P₂ decomposes faster than Mg₃As₂). Both crystallize in structure type D5₈ (carbon sesquioxide). d (Mg₃P₂) 2.055; (Mg₃As₂) 3.148.

**REFERENCES:**


Magnesium Carbides

\( \text{MgC}_2, \text{Mg}_2\text{C}_3 \)

These compounds cannot be prepared from carbon and the metal since \( \text{MgC}_2 \) decomposes below 500°C and \( \text{Mg}_2\text{C}_3 \) above 700°C. However, relatively pure products are obtained by passing gaseous hydrocarbons over heated MgO powder (60 microns or smaller). Prior to use, this extremely fine powder is activated by heating under vacuum for a short period of time.

I a. To prepare \( \text{MgC}_2 \), about 8 g. of Mg powder is placed in a 10-cm.-long iron boat and covered with some steel wool. The boat is then inserted into a porcelain tube of about 4 cm. diameter. The air is displaced by repeated evacuation and filling with \( \text{H}_2 \). The tube is then heated at 700°C for 40 minutes while a slow stream of \( \text{H}_2 \) is passing through it and cooled to 450°C at 11 mm. over a period of 10 minutes. Finally, acetylene is introduced over a period of 15 minutes, until atmospheric pressure is restored. Passage of \( \text{C}_2\text{H}_2 \) is then continued for one hour at a flow rate of 6 liters/hour and a temperature of 450°C. The tube is then removed from the furnace and cooled in a slow \( \text{H}_2 \) stream. The steel-blue to black, very hard product is ground at once under absolutely dry ether and stored. The crude carbides are purified by dissolving the excess Mg with ethyl bromide in ether, which may be done in a small Soxhlet extraction apparatus. A product containing 70% \( \text{MgC}_2 \) is obtained.

I b. The preparation of \( \text{Mg}_2\text{C}_3 \) is similar. As above, the air is displaced from the reaction tube, which is then heated to 850°C for one hour. After lowering the temperature, pentane is passed at 700°C for two hours and 710°C for one hour, under slightly reduced pressure (aspirator suction). The pentane is introduced into the reaction tube by means of a dropping funnel. A gas flow rate of 2.5 liters/hour corresponds to 35 ml., or 30 drops per minute. Cooling in a \( \text{H}_2 \) stream is carried out as above. The light to dark-gray products contain up to 85% \( \text{Mg}_2\text{C}_3 \).

Other preparative methods: II. Reaction of \( \text{MgCl}_2 \) with \( \text{CaC}_2 \) (does not, however, result in a purer product), III. Reaction of a ether solution of diethylmagnesium and acetylene.

Properties:

\( \text{MgC}_2 \) has a tetragonal and \( \text{Mg}_2\text{C}_3 \) a hexagonal structure. \( \text{MgC}_2 \) decomposes at about 550°C, forming \( \text{Mg}_2\text{C}_3 \) and C; \( \text{Mg}_2\text{C}_3 \) decomposes at 740 to 750°C into its elements. On reaction with water, \( \text{MgC}_2 \) and \( \text{Mg}_2\text{C}_3 \) give \( \text{C}_2\text{H}_2 \) and \( \text{C}_3\text{H}_4 \), respectively.

References:


Magnesium Silicide

\[ \text{Mg}_2\text{Si} \]

I. \[ 2\text{Mg} + \text{Si} = \text{Mg}_2\text{Si} \]

An intimate blend of Mg filings and pulverized Si (3 : 1) is charged into a MgO boat and heated under high vacuum. The reaction begins at 450°C, lasts only a few minutes, and is accompanied by a large volume increase. The product contains an excess of free Mg, but no free Si. The metal can either be distilled off at higher temperature (700°C) or extracted by treating the pulverized alloy with ethyl iodide in the presence of anhydrous ether, or with an ether solution of bromobenzene containing a grain of iodine. After washing with ether, the product is first dried at room temperature, then at 300°C. The slate-blue, shiny crystals have the composition \( \text{Mg}_2\text{Si} \).

II. \[ \text{SiO}_2 + 4\text{Mg} = \text{Mg}_2\text{Si} + 2\text{MgO} \]

When larger amounts of silicide are required for the synthesis of silanes, the compound is best prepared as follows:

Precipitated silicic acid, free of P and S and containing 0.3 to 0.5% (based on the weight of the anhydrous material) alkaline residue after evaporation is dehydrated by heating at bright red heat for several hours. The carefully pulverized anhydride is intimately blended with twice its amount of Mg powder. This mixture (100 g.) is ignited in an iron crucible of about 1000 ml. capacity, which is well cooled by a large quantity of cold water; the reaction rapidly propagates throughout the entire mass, generating incandescent white heat. Immediately after the onset of the reaction, the crucible is covered with a lid equipped with a gas inlet tube, and a fast \( \text{H}_2 \) stream is passed over the reactants. Some \( \text{Mg} \) is forced outside and burns on the lid. After cooling, the product cake adhering to the bottom of the lid can be easily removed.

Other preparative methods: III. Claims have been advanced that high purity \( \text{Mg}_2\text{Si} \) can be prepared by melt electrolysis of magnesium silicate.
PROPERTIES:

Rather hard, very brittle, slate-blue crystals. Crystallizes in structure type Cl (fluorite type). d 1.94. Stable to alkalis. Decomposed by acids, forming silicon hydrides and hydrogen.

REFERENCES:


Magnesium Germanide

\[ \text{Mg}_2\text{Ge} \]

48.6 72.6 121.2

A homogeneous mixture of finely powdered Ge and Mg (3:2) is introduced into a Pyrex tube. The latter is heated by means of a Bunsen burner, while a flow of H\(_2\) is passed through. The temperature is raised gradually. As red heat is approached, an incandescent reaction sets in at one spot and then spreads through the whole mass without further heating.

PROPERTIES:

Dark gray granular product. Characteristic odor of GeH\(_4\) due to reaction with air moisture. M.p. 1115°C.

REFERENCES:


Calcium, Strontium, Barium Metals

The available methods of preparation include: I) fusion electrolysis; II) aluminothermic reaction; III) decomposition of azides. The first method (used exclusively in industry) has only occasional laboratory application. Relevant literature references for Ca are listed under I. Method II does not give good yields with Ca, but is
applicable to Sr and Ba. Method III does not yield pure metal and may be used only with small quantities of material, since explosions are possible. The large surface area of the finely divided metal obtained by this method may be useful for special purposes. The procedures for Sr and Ba are similar to those given for Ca.

**CALCIUM, Ca**

In most cases commercial metal, purified by distillation, is used as the starting material.

*Purification by distillation:* a) Ca is distilled in an iron tube by directing metal vapor against a steel, nickel or copper cooling finger, which is polished at the lower end. A flange connects the pipe to a high vacuum system. Even better is an apparatus made of a quartz or porcelain tube $r$, sealed at one end and provided with a ground joint. A tall iron tubular crucible $t$ is inserted into the tube. The latter, reaching into the cold zone, provides protection against corrosion. The arrangement and dimensions are shown in Fig. 259.

For ease of disassembly the high vacuum connection should be made directly at the quartz tube $r$, rather than at the cap. The tube should thus be elongated accordingly. In such an arrangement the connection to high vacuum need not be broken while the distillate is being removed.

Crude Ca (40 g.) is placed in a crucible (1-mm.-thick walls) made of electrolytic iron, stainless steel or low-carbon steel. To prevent contamination of the distillate with a fine dust consisting of residual calcium oxide and calcium nitride, the metal is covered with a thin layer of steel wool. The latter is well degreased before use and ignited in moist $H_2$, as is the crucible, in order to effectively remove $P$ and $C$. The crucible must be separated from the round bottom of the quartz tube by a narrow porcelain piece $p$, so that it will not burst the tube on a sharp temperature change. A water-cooled, thin-wall finger $f$ runs axially through a 10-cm.-long glass tube passing through the ground cap. The rod is cemented.
to the tube with picein, forming an airtight connection. The metal parts must be perfectly smooth and free of oxide. The ground joint is cooled by means of a lead coil carrying water. The apparatus may be arranged vertically so that the cold finger will be suspended without stress in the guide tube of the ground cap. The same apparatus can, however, be operated more conveniently when tilted at about 30°. Aside from this the ground joints are easier to cool in this case.

Before it is put into operation, the apparatus should be tested for leaks under high vacuum. A good diffusion pump (with a capacity of 15-22 liters/sec.) should be in continuous operation in order to maintain a sufficiently high vacuum, since large volumes of gas contained in the crude material are evolved during distillation (especially in the initial stage). The pump is best connected to the apparatus by way of a trap cooled with liquid N$_2$. The tubing that connects the pump with the distilling apparatus should be as short and as large diameter as possible.

During the first phase of distillation, at 700°C, alkali metals (primarily Na, together with some Ca) are deposited upon the cold finger (Mg cannot be separated from calcium by distillation). The apparatus is allowed to cool somewhat and is then filled with purified Ar (or with dry CO$_2$ if completely cool). At the same time the cold finger and the ground cap are replaced by fresh ones. The alkali metals occasionally ignite on contact with the air when the apparatus is opened.

The main distillation step is carried out under high vacuum (≤10$^{-3}$ mm.) at the lowest possible temperature, so as to ensure high-purity metal. The last fraction is discarded. At 850°C the calcium deposit on the cold finger builds up as grape clusters of long silver-white, luminous crystallites, which will not tarnish to any appreciable extent on brief exposure to air. At higher temperatures the distillates obtained are richer in chlorine.

The structural characteristics of the separated metal depend markedly on the distillation rate. If the operating temperature is raised by 100-150°, the metal is deposited more rapidly and will be more compact. The temperature of the cold finger is likewise of importance. The lower the temperature, the smaller the particle size of the deposited metal. With air cooling of the finger the metal will separate in the form of rhombohedra.

After the thoroughly cooled apparatus has been filled with Ar or CO$_2$, the tube is opened and the metal dislodged from the cold finger with a spatula or, if necessary, with suitable tongs or forceps. This is best done under toluene or in a cylinder filled with CO$_2$.

It is advisable to repeat the distillation several times. The Ca obtained by this procedure is 99.7-99.9% pure and contains a few hundredths of one percent of O, N, Cl, Fe, Si, Mg.
Preparation of high-purity calcium by preliminary distillation followed by fractional distillation (2 mm. He) is described by W. J. McCreary, J. Metals 10, 615 (1958).

b) The procedure is simplified for lower purity metal. Use of the cold finger is omitted, as is the interruption of distillation for separation of alkali metals.

Crude Ca (20 g.) is placed in a tubular crucible made of low-carbon iron (inside diameter 20 mm., length 150 mm.) smoothly machined on the outside. An open iron pipe (length 150 mm.) smoothly machined on the inside, jackets the crucible with a clearance of only a few tenths of a millimeter. An iron wire is welded to the jacketing tube for more convenient handling. Both the crucible and the jacket must be well cleaned mechanically before the experiment and reduced in moist hydrogen.

The crucible and protective pipe are inserted into a quartz tube tilted about 30° from the horizontal. A ground cap connects the tube with a high-vacuum system. The distillation proceeds under the same conditions as described above. The iron jacket reaches up to the cooling coil. The temperature gradient along this cap is such that the alkali metals are deposited on its upper portion (which often results in ignition on opening of the reactor), while the Ca condenses in the form of beads somewhat below the height corresponding to the rim of the furnace. One of the disadvantages of this arrangement is that the condensation temperature of the calcium is sufficiently high so that the product reacts with the iron of the tube and thus becomes somewhat contaminated.

After cooling, the Ca is chipped off the wall with a chisel. This is best done when the pipe is cut open. If it is desired to compact the metal, the first crucible is removed and a shorter one substituted. This crucible has a larger diameter than the jacket, which dips into it. The Ca can then be melted down from the jacket in the same quartz reactor simply by shifting the furnace. It is best to melt under argon at atmospheric pressure, since too large quantities of the metal vaporize under vacuum.

c) A mild steel apparatus with a capacity of 200 g. of metal is used for distilling larger amounts of Ca.

Remelting: If compact Ca rather than a sponge is desired, the latter must be remelted. The pure distilled Ca (20–25 g.) is ground under Ar or CO₂ with an iron pestle in a crucible (diameter 23 mm., height 75 mm., wall thickness 1 mm.) made of electrolytic iron or low-carbon steel and preignited in moist H₂. A second crucible is fitted snugly into the first, pushed as far down as possible and welded to it at the rim level. The lower part of the outer crucible is cooled with water. The Ca melts at 900°C after brief heating. On cooling, the crucible is cut open and the compact Ca cylinder is easily loosened from the wall. The metal does not segregate, but the metal surface adhering to the rim absorbs a few
hundredths of a percent of Fe, which may be removed by turning the cylinder on a lathe.

PROPERTIES:

Atomic weight 40.08. Silver-white metal. M.p. 850°C, b.p. 1439°C, d 1.55. The m.p. is lowered considerably by nitrides and other impurities.

Calcium is as soft as Pb. The cubic face-centered $\alpha$-Ca transforms at 464°C into the hexagonal $\gamma$-Ca.

The $\beta$-Ca (between 300 and 464°C), until now considered a separate modification, is actually an alloy of Ca and impurities. The purer the metal, the more slowly it tarnishes in the air. It reacts rather slowly with water at ordinary temperatures, but the reaction becomes more vigorous on warming. With dilute acids, the reaction is violent.

REFERENCES:


b) Private communication from Prof. Dr. W. Fischer, Hannover.


STRONTIUM, Sr

I. Strontium can be prepared by fusion electrolysis (see references for calcium, part I), by the aluminothermic procedure (II), and by decomposition of azide (III). Strontium prepared by the aluminothermic process, as well as the commercially available metal, is purified by distillation under high vacuum.
17. ALKALINE EARTH METALS

II. $3\text{SrO} + 2\text{Al} = 3\text{Sr} + \text{Al}_2\text{O}_3$

927

310.9 53.9 262.9 101.9

Reaction II is endothermic. It goes to completion because the alkaline earth metals are highly volatile, and thus the equilibrium is continually and favorably shifted by the use of high vacuum.

The apparatus described above (Ca distillation) is charged with a homogeneous mixture of 60 g. of SrO, freshly ignited at $1100^\circ\text{C}$, and 14 g. of pure Al shot. Larger quantities of the reactants should not be used since the vigorous reaction will cause unnecessarily heavy losses through spattering. The mixture is preheated for an hour. The heating is then continued for four hours at $1010-1030^\circ\text{C}$ under high vacuum ($10^{-2}\text{ mm.}$). The reduction to powder and the mixing should be done rapidly, so as to keep the oxide as free as possible from hydroxide and carbonate. In spite of these precautions, a temporary deterioration of the vacuum occurs during the heating from 500 to $800^\circ\text{C}$.

The yield of 98% pure metal is 20-30 g. Strontium reacts rapidly with atmospheric moisture. Consequently, all operations such as opening the apparatus, Sr transfer, etc., should be done in an atmosphere of dry $\text{CO}_2$ or, better, under purified Ar.

The arrangement for distillation of commercial Sr is also the same as in the Ca procedure. Forty grams of crude Sr can be distilled in four hours at $1030^\circ\text{C}$. Repeated distillation yields 99.9% pure metal.

III. $\text{Sr(N}_3\text{)}_2 = \text{Sr} + 3\text{N}_2$

171.7 87.6 84.1

This method is the same as described for Ba under III. It yields a finely divided black metal powder, which is strongly contaminated with nitride (>10%) and ignites immediately on exposure to air.

PROPERTIES:

Silver-white metal, softer than Ca. M.p. $757^\circ\text{C}$, b.p. $1364^\circ\text{C}$; d 2.6. Crystallizes in structure type Al.

Tarnishes in air (becoming yellow-brown) and is finally coated by a layer of white oxide. Finely divided Sr ignites on exposure to air.

REFERENCES:


General: See also references listed for Ca.
BARIUM, Ba

I. The procedures are the same as for Ca and Sr. The pure metal is obtained by repeated redistillation under high vacuum.

\[
3\text{BaO} + 2\text{Al} = 3\text{Ba} + \text{Al}_2\text{O}_3
\]

The directions for preparing this metal are the same as for Sr (II), with minor modifications: 72 g. of BaO, nearly free of peroxide, and 11 g. of aluminum shot are heated for one hour. The heating is continued for five more hours at 1100°C under high vacuum (10^{-2} \text{ mm.}). The yield is < 20 g. of 97–98% pure metal. Commercial BaO usually contains some Sr, which concentrates in the distilled metal. Of the three alkaline earth metals, Ba is the most reactive. Every precaution must be taken when opening the apparatus or transferring the metal, since the deposited metal is finely crystalline and easily ignites in the presence of traces of moisture, especially while being detached from the cold finger. The safest way is to carry out this step under toluene.

In purifying Ba by distillation, the directions given for Ca should again be followed. Forty grams of crude Ba may be distilled at 1050°C in four hours. Triple distillation yields 99.6% pure metal.

III. \[
\text{Ba(N}_3\text{)}_2 = \text{Ba} + 3\text{N}_2
\]

Small quantities of Sr and Ba can be obtained by decomposition of the corresponding azides under vacuum. The metals are obtained as finely divided, highly reactive black powders. They may be used in various reactions, which can be carried out directly in the equipment used for preparation. Their isolation, i.e., removal from the apparatus, is hardly possible, because on exposure to air these metals react immediately with ignition. Another problem is contamination of the metal with nitride (>10%) due to a side reaction of the type: \(\text{Ba} + 2\text{Ba(N}_3\text{)}_2 = \text{Ba}_3\text{N}_2 + 5\text{N}_2\). By subjecting the \(\text{Ba(N}_3\text{)}_2\) to rapid decomposition, the nitride content can be kept down to a low level.

The decomposition equipment consists of a distillation flask (250 ml.) which is connected to a manometer and a vacuum pump. To avoid excessive loss of metal by entrainment, a piece of glass wool is inserted into the outlet tube.

The flask is charged with 10 g. of the azide and sealed on top. After evacuating the flask, heat (small flame) is applied at one point. Occasionally an explosion occurs, accompanied by fire, and the flask of \(\text{Ba(N}_3\text{)}_2\) then becomes coated with a black metal film.
The decomposition begins at 160°C; that of \( \text{Sr}(\text{N}_3)_2 \) at 140°C. Once started, it can be carried to completion at a lower temperature (120°C for Ba and 110°C for Sr).

**PROPERTIES:**


On exposure to air Ba quickly turns gray and finally black. Ignites very readily and reacts very vigorously with water.

**REFERENCES:**


*General*: See references given for Ca and Sr.

### Calcium and Barium Hydrides

\[
\text{CaH}_2, \text{SrH}_2, \text{BaH}_2
\]

\[
\text{Ca (Sr, Ba)} + \text{H}_2 = \text{CaH}_2 (\text{SrH}_2, \text{BaH}_2)
\]

Following repeated redistillation under vacuum, the metal is milled free of the adhering oxide under argon. When the surface of the metal is clean and bright, it is placed in the hydrogenation apparatus described for the preparation of alkali hydrides (p. 971). Air must be excluded. Thoroughly purified and dried electrolytic \( \text{H}_2 \) is employed for the hydrogenation. The metal is placed in a boat made of pure electrolytic iron, which is inserted into a quartz tube connected to a manometer. A thin-wall tubular insert made of electrolytic iron is fitted into the quartz tube to protect its heated portion from chemical attack.

Hydride formation usually begins between 400 and 500°C for Ca and Sr and between 200 and 300°C for Ba. Thereafter the temperature is raised to 1000°C. As soon as the absorption of \( \text{H}_2 \) is completed, the reactor is slowly cooled. The hydride is now ready for use, provided air and moisture are absent.

The finely crystalline substances thus obtained resemble the mineral serpentine and retain the fibrous structure of the original metals. The interior of the \( \text{CaH}_2 \) product in most cases contains a residue consisting of unreacted Ca metal. As the temperature rises above 1000°C the compound, in a stream of \( \text{H}_2 \), becomes overheated and dissociation begins. The metal evaporates and the components recombine in the colder areas of the tube. However,
slow distillation yields the hydrides as colorless, lustrous crystals, about 1 mm. wide. A residue is left in the boat.

To arrive directly at very pure hydrides, a special apparatus is used. This is provided with a mechanical arrangement for continuous grinding of the reaction product as it is formed during the hydrogenation. W. D. Treadwell and J. Sicher, Helv. Chim. Acta 36, 1938 (1953), used such equipment to obtain nearly 99.9% pure CaH₂.

ANALYSIS:

The hydride samples are removed from the apparatus in the absence of air and moisture and are then decomposed with air-free water under vacuum. The H₂ formed in the decomposition is cooled to a low temperature to condense out the moisture. It is then dried over P₂O₅, transferred to a gas burette by means of a Toepler pump, and measured.

PROPERTIES:

Colorless, lustrous rhombic crystals, the stability decreasing from CaH₂ to BaH₂. The hydrides react vigorously with water, evolving H₂. The heats of formation from the elements are remarkably high.

\[ d (\text{CaH}_2) 1.90; \ (\text{SrH}_2) 3.27; \ (\text{BaH}_2) 4.15. \]

REFERENCES:


Calcium, Strontium, Barium Halides

The anhydrous halides of Ca, Sr and Ba are prepared in the same way as described for the corresponding compounds of Be and Mg.

Anhydrous iodides can also be obtained from the hydrides by using nonaqueous solvents as reaction media. In pyridine solution, for example, the reaction is: \( \text{BaH}_2 + 2\text{NH}_4\text{I} = \text{BaI}_2 + 2\text{NH}_3 + 2\text{H}_2. \)
Most of the pyridine is then distilled off and the residual, bound solvent is removed under vacuum at 150-160°C. The yield is 97%.

REFERENCE:

Calcium Oxide

CaO

I.

\[ \text{CaCO}_3 = \text{CaO} + \text{CO}_2 \]

100.1 56.1 44.0

Calcium oxide is obtained by igniting calcium carbonate or calcium oxalate at about 800°C.

Purification of calcium salts: Very pure calcium oxide, such as needed in the preparation of phosphorus, is obtained according to Tiede and Riemer in the following way:

Carrara marble is dissolved in very pure nitric acid. The CO\(_2\) is completely removed by boiling and the hot solution is treated with Ca(OH)\(_2\) solution to precipitate traces of salts of foreign metals (primarily Cu, Fe and Mg). The filtrate is heated almost to boiling and CO\(_2\) is passed through. The bicarbonate is formed in proportion to the amount of added Ca(OH)\(_2\) and is subsequently decomposed by boiling the solution until it is neutral. The Ca is finally precipitated as the carbonate, carrying along traces of Fe. The filtered Ca(NO\(_3\))\(_2\) solution is treated with a concentrated solution of pure (NH\(_4\))\(_2\)CO\(_3\) which contains one third by volume of concentrated ammonia. The CaCO\(_3\) precipitates on cooling. The precipitate is washed well, dried and ignited to the oxide. A quartz crucible and an electric furnace are used for this last reaction. For best results, no more than 2-3 g. should be prepared at a time.

Other methods: II. A purification procedure including an even greater number of steps is described in a thesis by Riemer. The process yields CaCO\(_3\) and CaO of extreme purity such as employed in the production of luminescent materials. III. Very pure CaCO\(_3\) is prepared according to the method of Richards and Honigschmid. Calcium nitrate solution is slightly acidified with nitric acid and treated with a slight excess of pure Ca(OH)\(_2\) solution to precipitate Fe(OH)\(_3\) and most of the Mg(OH)\(_2\). Impurities consisting of Ba, Sr and Mg salts are removed by repeated recrystallization of the nitrate. The (NH\(_4\))\(_2\)CO\(_3\) required for the precipitation of the carbonate is purified by distillation with water. Further details will be found in the original report.

PROPERTIES:


REFERENCES:


**Strontium Oxide**

\( \text{SrO} \)

I. Strontium oxide can be obtained by heating pure \( \text{SrCO}_3 \) in a stream of \( \text{H}_2 \) at 1300°C for several hours, by dehydration of \( \text{Sr(NO}_3\text{)}_2 \cdot 4\text{H}_2\text{O} \) with subsequent calcining at 1100°C for 1.5 hours, or by dehydration of \( \text{Sr(OH)}_2 \) above 850°C. If a high-purity product is desired the heating (as in the case of \( \text{BaO} \)) is done in a stream of \( \text{N}_2 \) or \( \text{H}_2 \), free of \( \text{O}_2 \) and \( \text{CO}_2 \). The vessels must be made of nickel or sintered alumina.

**Purification of strontium salts:** II. Highest purity \( \text{SrO} \) is obtained by way of the nitrate, which is prepared as follows. Strontium carbonate is treated with 500 ml. of distilled water in a five-liter flask. This suspension is slowly dissolved in 830–840 ml. of concentrated nitric acid. Next, 7 ml. of concentrated \( \text{H}_2\text{SO}_4 \) is added to precipitate most of the \( \text{Ba} \), and the solution is brought to boiling. The hot solution (pH ~3) is treated for 30 minutes with \( \text{H}_2\text{S} \), previously passed through \( \text{Ba(OH)}_2 \) solution. After the precipitate has settled, it is suction-filtered through a glass frit to avoid contamination of the filtrate with dust.

The filtrate is treated with 45 ml. of saturated ammonium oxalate solution and the Ca precipitated on addition of ammonia to a pH of 7. The mixture is brought to boiling and, while hot, treated again with \( \text{H}_2\text{S} \). It is left to stand overnight and filtered the next morning. Nitric acid is added until the pH is reduced to 3, and 2–3 ml. of \( \text{Br}_2 \) is added to oxidize Fe and Mn. Excess \( \text{Br}_2 \) is removed by boiling. The solution is then made alkaline with ammonia (pH 8) and \( \text{H}_2\text{S} \) is admitted briefly. After standing a few hours the solution is filtered and the filtrate is reacidified with nitric acid (pH 3). After heating to boiling, the filtration is repeated. The \( \text{Sr(NO}_3\text{)}_2 \) solution is by this time sufficiently free of heavy metal impurities.

III. The last traces of Ca and Mg can be removed by precipitating the Sr as \( \text{SrSO}_4 \). In most cases, however, repeated recrystallization (3 or 4 times) of strontium nitrate in Pt or quartz vessels will suffice. By passing very pure \( \text{NH}_3 \) and \( \text{CO}_2 \), Sr can be precipitated as \( \text{SrCO}_3 \) from a solution containing 200 g. of \( \text{Sr(NO}_3\text{)}_2 \cdot 4\text{H}_2\text{O} \) in one liter of water. The precipitate is washed 8 to 10 times by decantation. After filtration and drying in an electric furnace it is calcined to form the oxide.
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PROPERTIES:


REFERENCES:


**Barium Oxide**

**BaO**

I. Thermal decomposition of the nitrate (which melts and decomposes with effervescence), iodate or peroxide is used to obtain the oxide. The final temperature must be above 800°C. Normally the compound is heated in air to 1100°C, to remove any peroxide impurity present.

The highest purity product is obtained by thermal decomposition of BaCO$_3$ under high vacuum. The most expedient procedure is to liberate most of the CO$_2$ at 950°C and the remainder at 1100–1150°C. This prevents melting of the product.

Another method for preparing BaO is based on careful dehydration of Ba(OH)$_2$·8H$_2$O, which has been repeatedly recrystallized before use. The mass is then heated for two hours at 800°C in a stream of dry N$_2$ or H$_2$, free of O$_2$ and CO$_2$. Melting of the Ba(OH)$_2$ cannot be avoided since the temperature reaches 700°C; hence, it is advisable to use vessels made of sintered corundum or pure nickel. Other materials such as Pt, stainless steel, quartz, porcelain, etc., are corroded.

Purification of barium salts: II. Impurities which can be separated as sulfides are removed by following the directions given for SrO (II). The hydroxide octahydrate is not altogether suitable for further purification (removal of residual traces of Sr, Ca, Mg, etc.) since its recrystallization, while removing all traces of Ca, does not lead to complete removal of Sr. The nitrate, on the other hand (according to Richards), is very well suited for removal of the last traces of Sr, Ca, Mg, K and Na from Ba salts.
Very pure commercial barium nitrate is recrystallized eight times from very pure water in Pt containers. If Pt is not available, quartz vessels may be used. The mother liquor is separated by centrifuging in a Pt tube, this procedure being about ten times as efficient as suction filtration. At the beginning, as well as toward the end of the recrystallization process, the nitrate solution is filtered through a fine glass frit. Every precautionary measure to exclude dust and harmful vapors is observed during the procedure. The simplest way to achieve this is to use the particular laboratory premises for no other work but the above procedure.

To obtain BaCO₃ (as the starting material for various Ba salts), a hot, pure barium nitrate solution is precipitated, with (NH₄)₂CO₃, which is prepurified by distilling its aqueous solution through a Pt condenser into a Pt receiver. The BaCO₃ is separated from the mother liquor in a Pt centrifuge tube.

**PROPERTIES:**


Converted to the hydroxide by moisture. The carbonate is formed on exposure to the CO₂ of the air.

**REFERENCES:**


**Calcium Hydroxide**

Ca(OH)₂

Calcium hydroxide is formed on addition of water to CaO, provided the latter has not been overheated during calcination. Another way is to treat aqueous solutions of calcium salts with alkalies.

$$\text{Ca(NO₃)₂} \cdot 4\text{H₂O} + 2\text{KOH} = \text{Ca(OH)₂} + 2\text{KNO₃} + 4\text{H₂O}$$

I. Boiled water (500 ml.) is used to dissolve 46 g. of Ca(NO₃)₂·4H₂O. To this solution, 500 ml. of 1N C.P. potassium hydroxide solution (CO₂ free) is added in small portions with shaking, the temperature being kept at 0°C. The product is washed a number of times with a total of 12 liters of water, filtered and again washed on
the filter. The precipitate is dried for 20 hours under vacuum over sulfuric acid (d 1.355); it then has a composition corresponding to its formula.

In all of these procedures the CO₂ of the air must be carefully excluded.

II. Crystalline Ca(OH)₂ can be obtained by the diffusion method. Two 50-ml. beakers are placed in a vessel equipped with a removable lid. One of them contains 30 g. of recrystallized CaCl₂·6H₂O dissolved in 50 ml. of H₂O; the other contains 12 g. of NaOH in 50 ml. of H₂O and a small quantity of Ba(OH)₂ to precipitate the carbonate. Enough water is poured into the vessel to cover the beakers 2 cm. above the rim. After four weeks, the 1-cm.-long crystals are collected on a filter crucible and washed quickly with water, dilute hydrochloric acid, water, alcohol and ether. They are then dried for a short time at 110°C.

III. Small crystals can be obtained in a few hours by treating a Ca(OH)₂ solution, saturated at 10°C, with 20 ml. of 20% potassium hydroxide solution.

**PROPERTIES:**

Hexagonal crystals, which decompose before melting. At a water vapor pressure of 10 mm., the decomposition temperature is 380°C. Moderately soluble in water. d 2.08.

**REFERENCES:**

III. C. Nogareda, Anales Soc. Espanola Fisica Quim. 29, 556 (1931).

**Strontium Hydroxide**

Sr(OH)₂ · 8H₂O, SrO · 9H₂O

When SrO is moistened with the theoretical amount of water, a vigorous reaction occurs, with formation of Sr(OH)₂ (white powder) and evolution of heat. On further addition of water, the mono-, hepta-, or octahydrate is formed. Because of its low solubility, the octahydrate can be prepared from any soluble Sr salt by precipitating with a strong base.

\[
\text{Sr(NO}_3\text{)}_2 + 4\text{H}_2\text{O} + 2\text{KOH} + 4\text{H}_2\text{O} = \text{Sr(OH)}_2 + 8\text{H}_2\text{O} + 2\text{KNO}_3
\]

A solution containing 20 g. of Sr(NO₃)₂·4H₂O in 40 ml. of distilled water is cooled to 0°C and treated in the absence of CO₂ with
the equivalent amount of KOH dissolved in 100 ml. of H₂O. The alkali is added drop by drop. The precipitate is washed with 1.5 liters of H₂O and is then free of both K and NO₃ ions.

PROPERTIES:

Prismatic, tetragonal crystals. The first mole of water of crystallization apparently is more readily given off than the others. The dehydration curve shows that, at p = 10 mm. H₂O, Sr(OH)₂ is stable from 100 to 450°C. M.p. 375°C.

REFERENCE:


Ca₅₃, SrO₂, BaO₂

CaO₂ · 8 H₂O, SrO₂ · 8 H₂O, BaO₂ · 8 H₂O

CaO₂

In common with the corresponding magnesium compound, and in contrast to SrO₂ and BaO₂, CaO₂ cannot be obtained through direct reaction of O₂ with either CaO or Ca. It is found only by heating CaO₂ · 8H₂O above 130°C. Nearly anhydrous peroxide, CaO₂ · 0.38 H₂O, is obtained by direct precipitation from aqueous solutions, e.g., by treating 11 g. of CaCl₂ · 6H₂O, dissolved in 50 ml. of 3% H₂O₂, with 7 ml. of 25% ammonia in 100 ml. of H₂O. The temperature should either be above 60°C, or the amount of water should be reduced to 30 ml. at 20°C.

SrO₂

This compound is usually prepared by slow (several hours) dehydration of the octahydrate at 300°C. It can also be obtained, but not entirely water-free (0.68 mole of H₂O), by precipitating a solution of 5 g. of Sr(NO₃)₂ in 5 ml. of 30% H₂O with 7 ml. of 25% ammonia at 55°C.

Very pure SrO₂ can be prepared from SrO under an O₂ pressure of 200 to 250 atm. at 350-400°C. The starting material must be free from hydroxide or carbonate and the O₂ should be thoroughly dried.
BaO₂.

The peroxide is prepared by careful dehydration of the octahydrate, first in a desiccator under reduced pressure, and then in a drying pistol over P₂O₅ at 100°C.

According to Bernal et al., preparations containing 100% BaO₂ (or SrO₂) may be obtained only by drying for one month in O₂ at room temperature.

High grade BaO₂ can also be prepared by heating loose BaO at 500°C in a stream of O₂ which has been thoroughly dried and freed of CO₂.

PROPERTIES:

Formula weights: CaO₂ 72.08; SrO₂ 119.63; BaO₂ 169.36. Of the three peroxides (all white) BaO₂ is the most stable and its solubility in water is the highest. When immersed in water, the peroxides gradually form the octahydrates at room temperature. Decomposed by acids with liberation of H₂O₂. Both SrO₂ and BaO₂ crystallize in the tetragonal system. They are face-centered and are isostructural with CaC₂.

REFERENCES:


THE OCTAHYDRATES

The peroxide hydrates are formed when alkaline solutions of alkaline earth salts are treated with H₂O₂. To avoid the formation of dihydrates or of anhydrous salts, the following directions must be complied with when working with a Ca salt, for example: 11 g. of CaCl₂·6H₂O is dissolved in 5 ml. of H₂O and treated with 50 ml. of 3% H₂O₂. To this solution, 7 ml. of 25% ammonia in 100 ml. of H₂O is added.

The procedure is the same as for the preparation of SrO₂·8H₂O. At room temperature BaO₂·8H₂O is formed only in strongly alkaline solutions. An excess of H₂O₂ must be avoided. For example,
100 ml. of Ba(OH)$_2$ solution, previously saturated at 14°C, is treated with 5 ml. of 3% H$_2$O$_2$.

**PROPERTIES:**

Formula weights: CaO$_2$·8H$_2$O 216.20; SrO$_2$·8H$_2$O 263.75; BaO$_2$·8H$_2$O 313.48.

Lustrous, white crystals. The three compounds are isomorphous. In air, they become opaque and are slowly converted to the carbonates by the CO$_2$. They hydrolyze in water and are dehydrated in absolute alcohol.

**REFERENCES:**


C. Nogareda, Anales Soc. Espanola Fisica Quim. 28, 475 (1930).

**Calcium, Strontium, Barium Sulfides**

CaS, SrS, BaS

\[
\text{CaCO}_3 (\text{SrCO}_3, \text{BaCO}_3) + \text{H}_2\text{S} = \text{CaS} (\text{SrS}, \text{BaS}) + \text{H}_2\text{O} + \text{CO}_2
\]

100.1 (147.6, 197.3) 34.1 72.2 (119.7, 169.4) 18.0 44.0

Alkaline earth sulfides can be easily prepared in small quantities (3-5 g.) by heating their pure carbonates (C.P.) for about two hours at about 1000°C in a fast stream of an equimolar mixture of H$_2$S and H$_2$. When water ceases to evolve, H$_2$ alone is passed through for about half an hour to decompose the polysulfides. The product is left to cool in a stream of H$_2$.

Other preparative methods: Larger amounts of sulfides, though of lower purity, can be obtained by heating the carbonates in a crucible with an excess of elemental S. Here, tight closure of the crucible is essential and use of an autoclave is advantageous. This procedure is mostly used to produce phosphors based on alkaline earth sulfides.

**PROPERTIES:**

White powders (BaS is often grayish). M.p. > 2000°C, d CaS 2.59; SrS 3.65; BaS 4.36. Crystallize in structure type B1. Oxidize in dry air and are decomposed by moisture and, more rapidly, by acids, with which they evolve H$_2$S.
REFERENCES:


Calcium, Strontium, Barium Selenides

CaSe, SrSe, BaSe

1. $\text{CaSeO}_4, (\text{SrSeO}_4, \text{BaSeO}_4) + 4 \text{H}_2 = \text{CaSe (SrSe, BaSe)} + 4 \text{H}_2\text{O}$

\begin{center}
\begin{tabular}{cccccccc}
 & CaSeO$_4$ & (SrSeO$_4$, BaSeO$_4$) & + & 4H$_2$ & = & CaSe (SrSe, BaSe) & + & 4H$_2$O \\
 & 183.0 & (230.6 & 280.3) & 8.1 & 119.0 & 166.6 & 216.3 & 72.1 \\
\end{tabular}
\end{center}

Small quantities of alkaline earth selenides are obtained by the method of Berzelius, through reduction of the corresponding selenates in a H$_2$ stream. The water formed in this reaction decomposes the selenides, forming H$_2$Se. In turn, the latter is thermally cleaved into H$_2$ and Se, imparting a reddish hue to the preparation. It is therefore highly important to work with a fast H$_2$ stream and use only small amounts of starting material.

The selenates are prepared from the corresponding alkaline earth nitrates. The salt is added to a concentrated solution of K$_2$SeO$_4$ (H$_2$SeO$_4$ neutralized with potassium hydroxide). The precipitate is filtered off and dried at 200°C.

The selenate (about 1 g.) is distributed in a thin layer over a quartz boat 10 cm. long and 1 cm. wide. The drying at 200°C is repeated, this time in a reaction tube and in a stream of N$_2$. Reduction in a stream of H$_2$ follows. It should continue for two hours between 400-500°C for CaSeO$_4$, at 600°C for SrSeO$_4$, and at 500°C for BaSeO$_4$. A pure white product is obtained for SrSe and BaSe, but in the case of CaSe the white color occasionally shows a reddish tint.

To avoid undesirable decomposition caused by air moisture, transfer of the product from the boat must be carried out in the absence of air. Special devices are used for this purpose. These are connected to the reaction tube by means of ground-glass joints, so that the boat contents can be emptied into a side attachment (see Part I, p. 75).

II. $\text{SrSeO}_3 + 2\text{NH}_3 = \text{SrSe} + 3\text{H}_2\text{O} + \text{N}_2$

\begin{center}
\begin{tabular}{cccc}
 & SrSeO$_3$ & + & 2NH$_3$ & = & SrSe & + & 3H$_2$O & + & N$_2$ \\
 & 214.6 & 34.1 & 166.6 & 54.1 & 28.0 & & & & \\
\end{tabular}
\end{center}

Pure SrSe is best obtained from the selenite by high-temperature reduction with NH$_3$. The SrSeO$_3$ is prepared by dissolving repeatedly sublimed SeO$_2$ in water and adding the theoretical amount
of hot strontium nitrate solution (for a special method of purifying the salt, see Smith, Rosenstein and Ward). After neutralizing the solution with ammonia, the strontium selenite is filtered off, washed six times with water until free of nitrate, and dried at 200°C. The salt is reduced in a fast stream of NH$_3$ at 860°C. The reaction is completed in 2-3 hours.

When NH$_3$ is used as the reducing agent, side reactions take place.

Occasionally, N$_4$Se$_4$ forms in the colder portion of the tube and explodes when the boat is taken out.

The same method is used to prepare CaSe.

**PROPERTIES:**

White powders. d CaSe 3.82; SrSe 4.54; BaSe 5.02. Crystallize in structure type B1.

In air, the powders acquire a reddish color within a few minutes and turn light brown in a few hours. Decomposed by water. Treatment with HCl produces H$_2$Se gas, and red Se separates.

**REFERENCES:**


Calcium, strontium and barium tellurides, although not perfectly pure, can be obtained similarly by reduction of the tellurates in a hydrogen stream (CaTe at 680°C, SrTe at 690°C, BaTe at 580°C).

**REFERENCE:**

M. Haase, Z. Kristallogr. 65, 509 (1927).

**Calcium, Strontium, Barium Nitrides**

$\text{Ca}_3\text{N}_2, \text{Sr}_3\text{N}_2, \text{Ba}_3\text{N}_2$

$\text{Ca}_3\text{N}_2$

\[
3\text{Ca} + \text{N}_2 = \text{Ca}_3\text{N}_2 \quad \text{120.3} \quad 28.0 \quad 148.3
\]

Distilled, finely divided Ca metal is placed in a Ni boat and in a nitrogen stream for 3-4 hours at 450°C. At this temperature the
nitriding is particularly rapid, because the lattice of the metal becomes less compact as a result of structural changes in the crystals (transition point).

Contradictory data have been published on the nitriding temperature for Ca. The reaction has been reported to proceed at a measurable rate only above 800°C. The discrepancies, it seems, can be traced to use of metal which is not quite pure, or of N\textsubscript{2} still containing traces of O\textsubscript{2}.

Small amounts of Na vapor absorbed by the surface of the metal prevent the formation of a continuous nitride film; hence, they activate the metal. The latter, in the active form, is an agent for purifying argon; see p. 82.

When Ca metal is treated with NH\textsubscript{3} at 800°C, some hydride is formed simultaneously.

PROPERTIES:

\[ \alpha-\text{Ca}_3\text{N}_2 \text{ (structure type D5\textsubscript{3}) transforms into } \beta-\text{Ca}_3\text{N}_2 \text{ at } 700°C. \]

Depending on the temperature of formation the nitride powder is colored black (350°C) to golden yellow (1150°C), or else acquires mixed coloration (at intermediate temperatures). d 2.62. Decomposes in water to Ca(OH)\textsubscript{2} and NH\textsubscript{3}.

REFERENCES:

F. W. Dafert and R. Miklauz, Monatsh. Chem. 34, 1685 (1913).

Sr\textsubscript{3}N\textsubscript{2} and Ba\textsubscript{3}N\textsubscript{2}

The nitriding temperatures for Sr and Ba are 460 and 560°C, respectively. To achieve complete conversion to the nitride, the heating must be continued for a long time or the temperature must be raised to 700-750°C on cessation of absorption of N\textsubscript{2}.

REFERENCES:

F. W. Dafert and R. Miklauz, Monatsh. Chem. 34, 1685 (1913).
Barium Azide

\[ \text{Ba(N}_3\text{)}_2 \]

\[
2 \text{NaN}_3 + 2 \text{H}_2\text{SO}_4 = 2 \text{NaHSO}_4 + 2 \text{HN}_3
\]

\[
130.0 \quad 196.2 \quad 240.2 \quad 86.0
\]

\[
2 \text{HN}_3 + \text{Ba(OH)}_2 = \text{Ba(N}_3\text{)}_2 + 2 \text{H}_2\text{O}
\]

\[
86.0 \quad 171.4 \quad 221.4 \quad 36.0
\]

Hydrazoic acid is formed on dropwise addition of sulfuric acid (1 : 1) to NaN\(_3\) solution. The acid is next distilled into a receiver, which contains a Ba(OH)\(_2\) suspension (2/3 of the calculated amount). The distillation temperature should be about 60°C (or lower, if the pressure is reduced). A few drops of phenolphthalein are added to the reaction mixture and, toward the end of distillation, the remaining Ba(OH) is added continually to a neutral reaction (disappearance of red color). The work must be done under a good hood (strong draft), because the HN\(_3\) vapor is highly toxic.

Another way of preparing the azide is to place the entire quantity of Ba(OH) in the receiver and use a higher dilution. The excess of hydroxide is then removed by passage of CO\(_2\), and the precipitated BaCO\(_3\) is filtered off.

The Ba(N\(_3\))\(_2\) solution is crystallized in a vacuum desiccator over CaCl\(_2\). The resultant monohydrate is completely dehydrated over P\(_2\)O\(_5\). A preliminary recrystallization of the salt is advisable.

The strontium salt is prepared by a similar procedure.

**Properties:**

Crystallizes in cylindrical crystals. On impact, explodes with mild force, bursting into flames. \(d\) 2.94.

**Reference:**


Calcium Phosphide

\[ \text{Ca}_3\text{P}_2 \]

\[
3 \text{Ca} + 2 \text{P} = \text{Ca}_3\text{P}_2
\]

\[
120.2 \quad 62.0 \quad 182.2
\]

To prepare this salt, distilled Ca is heated with red P in a thoroughly evacuated combustion tube. The heating is continued
until the reaction becomes spontaneous. This is accompanied by incandescence. Milder reaction conditions result in a higher quality product. To this end, Ca is heated to dull red heat in a corundum boat, and P is slowly distilled onto the Ca. After cooling, the sealed end of the tube is broken off, and the tube is filled with dry CO₂, using the same procedure as described for Mg₃P₂ (II).

To ensure that no excess metal remains in the preparation, the product must be heated again with P for a long time at 600°C. An evacuated, sealed tube is used for this purpose.

Where purity requirements are particularly high, Ar should be used as carrier gas, following the directions given for Mg₃P₂ (I).

II. \[3 \text{Ca}_3(\text{PO}_4)_2 + 16 \text{Al} = 3 \text{Ca}_3\text{P}_2 + 8 \text{Al}_2\text{O}_3\]

93.1 43.2 54.7 81.6

If Ca₃P₂ is to be used only as a raw material for the preparation of PH₃, it can be prepared by the aluminothermic method. The drawback of this procedure is that the product phosphide cannot be separated from the Al₂O₃.

Powdered, predried calcium phosphate (232 g.) and 108 g. of Al shot are ground to a homogeneous mixture. An igniting mixture is used to kindle the reaction. In most cases it is necessary to preheat the crucible to 500°C.

PROPERTIES:
Crystalline, red-brown powder. d 2.51. Decomposes slowly in moist air and more vigorously in water yielding Ca(OH)₂ and PH₃.

REFERENCES:

Calcium Carbide
CaC₂

The CaC₂ obtained on reversal of the reaction producing CaCN₂ or on heating a mixture of CaCN₂ and C under high vacuum is much purer than that from the synthesis from the elements or the reaction between CaO and C.

I. \[\text{CaCN}_2 + C = \text{CaC}_2 + \text{N}_2\]

80.1 12.0 64.1 28.0
\[ 2 \text{CaCN}_2 = \text{CaC}_2 + 2 \text{N}_2 + \text{Ca} \]

A sintered clay boat is charged with pure CaCN\textsubscript{2}, either alone or with an added amount (somewhat below the calculated value) of well-charred sugar charcoal or acetylene black. The boat is inserted into a ceramic tube (inside diameter 30 mm., length 500 mm.). The tube is provided with a ground stopper at one end and sealed at the other. It is connected to a high-vacuum system and heated by means of an electric furnace with a molybdenum wire winding to temperatures above 1350°C.

The cyanamide (or the mixture with carbon) is heated in two stages. The first heating is continued for 2-3 hours at 1100-1150°C to remove most of \text{N}_2, which is drawn off under high vacuum. It is imperative that the temperature does not exceed 1170°C, since this is the eutectic temperature for the system CaCN\textsubscript{2}-CaC\textsubscript{2}. By that time the cyanamide is so far decomposed that mixed crystals of CaC\textsubscript{2} and CaCN\textsubscript{2} cannot be formed during the second heating stage at a higher temperature (1350°C, one hour), and thus the last traces of \text{N}_2 are quantitatively expelled. The product is pure white and contains over 99% CaC\textsubscript{2}, with no impurities, except traces of CaO and C.

The very slight corrosion of the Al\textsubscript{2}O\textsubscript{3} boat by the CaCN\textsubscript{2} cannot be entirely avoided. However, the loosely adhering product layer is easily detached.

Ⅱ. \[ \text{CaO} + 3 \text{C} = \text{CaC}_2 + \text{CO} \]

Laboratory preparation of calcium carbide via the reaction of pure CaO with very pure carbon in an electric arc at 2000°C is carried out as follows.

A large porcelain crucible, at least 80 mm. in diameter on top and 60 mm. high, is filled with a well-blended, dry mixture of equal parts of quicklime and wood charcoal to a level 10 cm. below the rim. The ingredients are not too finely powdered to prevent elutriation losses during later gas evolution. The crucible is placed on top of a brick. Two carbon rods (carbon welding electrodes, or rods made of electrolytic graphite), at least 15 mm. in diameter and 200 mm. long, are tapered to a point at their lower ends, while slotted (and thus flexible) brass caps are affixed on their upper ends. Each cap has a clamp screw, which serves as an electric terminal. A horizontal hole is drilled through each carbon rod and cap combination, and a 1-2 mm. connective copper wire is fitted snugly into the hole and bent back at both ends so that the cap is securely attached to the electrode. The electrodes are attached to a stand in such a way that they reach
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down to the center of the crucible, and their points are about 10 mm. apart. The asbestos insulated clamps connecting the electrodes to the stand are attached just below the brass caps. The lime-charcoal mixture is piled up in the center of the crucible and the latter is then covered with an asbestos sheet. Insulated copper wires (cross section 16 mm.) connect the electrodes to the power supply. The electrodes are in series with 0-50 amp. ammeter, a 40 amp. rheostat (6 ohms at 220 v., 3 ohms with a line voltage of 110 v.) and a double-pole knife switch. Where a suitable rectifier is available the use of direct current is preferred since a D.C. arc is far smoother than an A.C. arc. The potential across the electrodes is measured with a voltmeter.

The current is switched on with the rheostat set at maximum. It takes some time before the electric arc is initiated. The current is then set at 30-40 amp. The voltmeter should register a potential of 50-70 v. If the reading is much higher, the carbons are too far apart (and vice versa). The current must be shut off before any adjustment is made. When the operation is properly conducted, long tongues of burning CO escape from the crucible together with occasional puffs of dust from the charge. The current is shut off after 5-10 min. and the crucible is left to cool. A few grams of sintered or lump calcium carbide will be found under the electrode ends.

**Other methods:** III. Heating distilled Ca metal with C produces dark-colored or black carbides which are 94% pure, at best. IV. Technical grade carbide, 75-89% pure, can be enriched to 92% grade (containing residual Ca and C) by remelting a number of times at 2100°C, separation of strata, and compressing.

**PROPERTIES:**

When pure, colorless and crystalline. M.p. ~2300 C; d 2.22. The structure of pure CaC$_2$ differs from that of the commonly used "technical" carbide which is contaminated with impurities (pseudo-cubic, tetragonal, face-centered). Decomposes in water, evolving acetylene.

**REFERENCES:**

II. W. Fischer, private communication; see also H. Grubitsch, Praparative Anorganische Chemie, Vienna, 1950, p. 333.
(1937); see also H. H. Franck and H. Endler, Z. phys. Chem. (A) 184, 127 (1939).


**Calcium Cyanamide**

\[
\text{CaCN}_2
\]

\[
\text{CaCO}_3 + 2 \text{HCN} = \text{CaCN}_2 + \text{CO} + \text{H}_2 + \text{CO}_2
\]

Pure CN, previously dried over CaCl\(_2\) and P\(_2\)O\(_5\), is condensed in a receiver cooled to a low temperature. The amount used is three times the stoichiometric quantity. A stream of N\(_2\) is bubbled, preferably mixed with NH\(_3\), through the receiver and becomes laden with HCN. It is then passed over CaCO\(_3\), which fills a porcelain boat inserted into a porcelain tube. The cooled HCN receiver is warmed to 18°C when a reaction temperature of 700 to 850°C is reached in the porcelain tube, but not before. Heating for three hours yields a perfectly white, 99.4% pure product (34.8% N).

**PROPERTIES:**

Colorless crystals. M.p. ~1200°C. Gradually decomposed by water. Simultaneous treatment with CO\(_2\) and water liberates free cyanamide. Warming a cyanamide solution to 70°C yields urea.

**REFERENCE:**


**Calcium Silicides**

\[
\text{CaSi, CaSi}_2
\]

\[
\text{Ca} + \text{Si} = \text{CaSi}
\]

A mixture of Ca chips and pure Si (15% excess) is placed in a boat made of unglazed hard porcelain. The boat is immediately pushed into the hot (1000°C) zone of a quartz tube through which a CO\(_2\) stream is passed. Within a few seconds a vigorous reaction
sets in and the mass begins to melt. The boat is then withdrawn from the hot zone, thus immediately quenching the product. When crushed to a powder, the grayish-black, porous, solid mass disintegrates into CaSi flakes, which have a metallic luster. The thin crust of CaO is easily removed.

**PROPERTIES:**

Covering CaSi with dilute hydrochloric acid causes vigorous decomposition. Spontaneously igniting silanes are formed, with white silicic acid as the residue.

\[
\text{CaSi}_2
\]

I.  
\[
3 \text{ CaO} + 5 \text{Si} = 2 \text{CaSi}_2 + \text{CaSiO}_3
\]

Following Goldschmidt's procedure, \(\text{CaSi}_2\) is prepared by fusing high purity \(\text{CaO}\) (53.6%) and \(\text{Si}\) (26.4%) in the presence of suitable fluxes (12% \(\text{CaF}_2\) and 8% \(\text{CaCl}_2\)) at 1400°C. The melt must be thoroughly stirred with an \(\text{Al}_2\text{O}_3\) rod so that the molten \(\text{CaSi}_2\) will separate on the surface of the melt. The hot, viscous reaction mixture disintegrates on cooling, freeing silicide particles. The product obtained by this method is always rich in Si.

Larger charges result in improved yields.

II. Simple fusion of the elements does not produce pure \(\text{CaSi}_2\). Therefore, for smaller quantities and higher purity, it is preferable to heat CaSi with the stoichiometric amount of Si.

\[
\text{CaSi} + \text{Si} = \text{CaSi}_2
\]

The mixture is placed in a Ni boat and heated in a stream of \(\text{H}_2\) at 1000°C. The last phase of conversion proceeds very slowly and requires up to 15 hours of heating.

**Other methods:** \(\text{CaSi}_2\) can also be prepared, according to Dodero, by melt electrolysis above 1000°C using a flux. The proportions of the components are: \(3\text{SiO}_2 + 3\text{CaCO}_3 + 6\ \text{CaF}_2 + \text{CaCl}_2\).

**PROPERTIES:**

Hexagonal lead-gray tablets, with a bright metallic luster. M.p. 1020°C; d 2.5. Crystallizes in structure type C12. If not sufficiently cooled with ice, reaction with HCl is violent and the disilicide dissolves while a characteristic greenish-yellow product separates out.

For the preparation of strontium and barium silicides, see Wöhler and Schuff. The reaction proceeds as in the case of calcium silicide, through at a somewhat higher temperature.
REFERENCES:

L. Wöhler and F. Müller, Z. anorg. allg. Chem. 120, 49 (1922).

**Calcium Germanide**

CaGe

I.  \[ \text{Ca} + \text{Ge} = \text{CaGe} \]

40.0 72.6 112.6

Calcium turnings are ground to a fine powder in a ball mill under anhydrous benzene. Traces of benzene are then removed under vacuum.

Using the method described on p. 712, GeO_2 is reduced to metal powder with the aid of H_2.

The metal powders are mixed in stoichiometric proportions in an alundum boat. The boat is placed in an evacuated quartz tube and the reaction is started by bringing the boat contents to red heat. Suddenly a bright glow appears at one spot, spreading within seconds throughout the boat and causing partial pulverization of its contents. The reaction is finished at that point, but the product still contains some unreacted Ge. This happens even when an excess of calcium is used.

II.  \[ \text{CaH}_2 + \text{Ge} = \text{CaGe} + \text{H}_2 \]

42.0 72.6 112.6 22.4

Germanium powder is mixed with an equimolar quantity of CaH_2, previously pulverized under N_2 blanket. The hydride is taken in slight excess. The mixture is placed in an iron boat and the latter inserted into an electrically heated ceramic tube. The atmosphere within the tube is inert at that point. The tube is then connected to a high-vacuum system. The reaction begins at about 450°C and is finished at about 950°C, provided the H_2 formed in the process is removed at regular intervals. The temperature is then raised to 1000°C and gas removal continued for another half hour to achieve complete removal of the last traces of H_2. After cooling under vacuum, the tube is opened and the product is pulverized as rapidly as possible and placed in sealed ampoules. It still contains traces of Ca.
PROPERTIES:

Dark-gray powder. Rapidly turns yellow on exposure to atmospheric moisture.

REFERENCES: